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CATION EXCHANGE FOR AMMONIA REMOVAL FROM
WASTEWATER

Master of Science Thesis

Thesis supervisor:

Raghida Lepistö, Dr. Tech., Adjunction professor
Tampere University of Technology
Department of Chemistry and Bioengineering

ABSTRACT

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The pollution of surface and ground waters by nitrogen (N) is a common problem. Anthropological sources of N in water are from animal farms, untreated municipal, industrial, and agricultural wastewater, which has elevated the eutrophication of lakes, estuaries and rivers. N species in the environment can impact also on human, animal, and plants wellbeing. Ammonia (NH_3) is the initial indicator of N pollution and exists as ammonium (NH_4^+) and ammonia ($\text{NH}_3(\text{aq.})$) in water.

This work studied the use of ion exchange (IE) to remove NH_3 from the wastewater (bioslurries) using natural adsorbent material (zeolite). IE experiments were conducted in two phases. In phase one, batch experiments were carried out to study the effects of NH_4^+ load, pH, solids, contact time, and particle sizes (0.2-0.5 & 0.6-2.0 mm) on NH_3 removal capacity of zeolites. The exchange kinetics and isotherms of both zeolite particles were determined using data obtained from NH_4^+ load studies. In phase two, column experiments were used to study the effect of flow rates, pH, and regeneration on NH_4^+ removal capacity of zeolite to determine the feasibility of the process in natural environment.

In both experimental methods (batch and column), NH_3 adsorption capacity (Q) was significantly high with 0.2-0.5 mm compared to 0.6-2.0 mm particle size zeolite, because 0.2-0.5 mm had greater specific surface area and shorter diffusion path.

The batch studies showed that the initial NH_4^+ Q increased with increased concentration of NH_4^+ in solution. NH_4^+ adsorption was rapid at the beginning of the experiment as all the adsorption sites were empty and maximum adsorption took place within the first 10 minutes of the experiment time. The pH effect was studied at pH range 6 to 8.5 with 0.2-0.5 mm zeolite. At this pH range, the pH had minimal effect on the NH_4^+ removal capacity of the zeolite. The kinetic analysis showed that the adsorption of NH_4^+ on both zeolite types at different NH_4^+ concentrations followed the pseudo second order model indicating sorption capacity is proportional to the number of activated sites occupied on the sorbent. Equilibrium isotherm data were fitted to the linear Langmuir and Freundlich models.

The batch experiments were also performed to study the effect of total solids (TS) on NH_3 removal capacity of the zeolite. NH_3 Q and removal efficiency (E%) of both zeolite types decreased with an increase in TS concentration in the solution due to interference of the solids with the IE process.

The column studies showed that the lower flow (10 ml/min) rate had maximum NH_3 removal capacity compared with the higher flow rate (50 ml/min) as low flow rate provided more contact time between zeolite and the solution. The pH effect was studied at pH range 6.5 to 9.5. The NH_3 Q was more or less the same at the pH range of 6.5 to 8.0 and decreased sharply at pH 9.5 due to N-species distribution and partial dissociation of zeolite.

The column regeneration experiments showed that 0.5M NaCl was better than HCl regeneration. NaCl regeneration can efficiently regenerate exhausted zeolite and even after 6th regeneration cycle, NH_4^+ E% of zeolite was not affected. On the other hand, regeneration with HCl showed that HCl was not able to regenerate exhausted column, it was probably due to competition between NH_4^+ and H^+ ions at lower pH.

In conclusion, this study showed that N in raw bio-slurries can be efficiently removed with IE and natural zeolite. However, bio-slurries are usually characterized with high solid contents, which can hinder the application of IE to such medium in large-scale application. Further studies are needed to determine the best approach for sustainable IE application for N removal from liquid bio-wastes, e.g., combined with pretreatments.

PREFACE

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ABBREVIATIONS AND SYMBOLS

Al	:	Aluminium
Al ₂ SiO ₅	:	Aluminium Silicate
Ca	:	Calcium
C _d	:	Cadmium
C _e	:	Equilibrium concentration of ammonium in the solution
C _t	:	Concentration of ammonium at time t
CEC	:	Cation exchange capacity
Cl	:	Chlorine
Ca(OH) ₂	:	Calcium hydroxide
CO ₃	:	Carbonate
COOH	:	Carboxyle group
CO(NH ₂) ₂	:	Urea
Cu	:	Copper
DI	:	Deionized water
EU	:	European Union
EPA	:	Environmental Protection Agency
E%	:	Removal efficiency
Fe	:	Iron
H	:	Hydrogen
H ₂ O	:	Water
H ₂ SO ₄	:	Sulfuric acid
H ₃ BO ₃	:	Boric acid
HCl	:	Hydrochloric acid
HCO ₃	:	Bicarbonate
IAEA	:	International Atomic Energy Agency
IE	:	Ion exchange
ISA	:	Ionic Strength Adjuster
K	:	Potassium
K _b	:	Ammonium ionization equilibrium constant
K _w	:	Ionization constant of water
k ₁	:	Rate constant of pseudo-first-order model
k ₂	:	Rate constant of pseudo-second-order model
K _f	:	Freundlich constant
K _L	:	Langmuir constant
Mg	:	Magnesium
MQ	:	Milli-Q
mV	:	millivolts
N	:	nitrogen
N ₂	:	dinitrogen
NH ₂ Cl	:	monochloramine
NHCl ₂	:	dichloramine
NH ₄ NO ₃	:	ammonical nitrate
NCl ₃	:	trichloramine
NH ₃	:	ammonia
NH _{3(aq)}	:	ammonia in water
NH ₄ ⁺	:	ammonium

$\text{NH}_4\text{H}_2\text{BO}_3$:	Ammonium borate
NO_3	:	nitrate
NO_2	:	nitrite
N_2O	:	nitrous oxide
NO	:	nitric oxide
Na	:	Sodium
NaCl	:	Sodium Chloride
NaOH	:	Sodium hydroxide
O	:	Oxygen
OH	:	Phenol group
ON	:	Organic nitrogen
Pb	:	Lead
PO_4	:	Phosphate
Q	:	Adsorption capacity
q_{max}	:	Maximum uptake of ammonium
q_e	:	Equilibrium amount of ammonium exchange by zeolite
q_t	:	Amount of ammonium adsorbed at time t
R_L	:	Separation factor
S	:	Cross-section area
SD	:	Standard deviation
Si	:	Silica
TS	:	Total solids
t	:	Time
v	:	Filtration rate
V	:	Volume of sample
WHO	:	World Health Organisation
WFD	:	Water Framework Directive
Zn	:	Zinc
ϵ	:	porosity
ρ_b	:	particle density
$1/n$:	Heterogeneity factor

1. INTRODUCTION

Demand of water for drinking and other uses are increasing day by day. To be able to fulfill growing demand, we need to keep water resources clean and pollution free. However, water resources management and keeping it pollution free is a big challenge as a result of rapid industrialization, urbanization and population growth. Industries, agriculture, and municipalities produce huge quantity of wastewater which contains pollutants such as such anions, cations, oils, and wide range of organics (Wang & Peng, 2010) which are harmful to the aquatic and terrestrial animals. Thus, pollutants in wastewater must be removed before discharging it into soils and water resources.

Deterioration of water quality all over the world is a serious environmental problem. Of particular concern is the wastewater containing nitrogenous compound. Nitrogenous compound is commonly present as organic nitrogen (ON), ammonia (NH_3), nitrate (NO_3^-) or nitrite (NO_2^-) compounds in wastewater (Farkas et al, 2005). Generally, wastewater contains approximately $15\text{--}50\text{ mg/dm}^3$ of nitric compounds of which 55–60% is NH_3 and 40–50% is organic form of protein, pesticides, and amino acids (Zabochnicka & Malinska, 2010). Therefore, NH_3 is one of the common toxic pollutants in wastewater and is present in untreated sewage, industrial wastewater discharge, and landfill leachates.

NH_3 is present either as ammonium (NH_4^+) or ammonia ($\text{NH}_{3(\text{aq})}$) in water. The excessive amount of NH_3 in water streams lead to eutrophication and depletion in dissolved oxygen and corrosion or biological fouling in industrial waste system (Widiastuti et al, 2011). Different methods can be used to remove NH_3 from wastewater such as breakpoint chlorination (Erdogan & Ulku 2011), biological processes (nitrification and denitrification), air stripping, chemical treatment and selective ion exchange (IE) (Erdogan & Ulku 2011; Sarioglu, 2005; Ji et al, 2007; Demir et al, 2002). The classical method of NH_3 removal from wastewater is biological process. However, biological process is not the best option for shock loads of NH_3 as unacceptable peaks may appear in the effluent NH_4^+ concentration (Huang et al, 2010; Karadag et al, 2006). In addition, biological process needs additional carbon source for removal of NH_3 from low organic content which may add to the treatment cost (Huang et al, 2010).

The alternative to biological process is IE. IE method usually employs organic resin which is very selective but too expensive. Hence, the particular ion exchanger of interest in this study was zeolite as it is abundant in nature and cheap. Natural zeolites are the most important inorganic ion exchangers as they exhibit high IE capacity, selectivity, and compatibility with the natural environment (Sarioglu, 2005; Ji et al, 2007). Besides, NH_3 removal using natural zeolite is very simple in operation and applications (Huang et al, 2010; Demir et al, 2002; Englert & Rubio, 2005).

Several researches have been carried out to study NH_3 removal from wastewater using zeolite (Sarioglu, 2005; Erdogan & Ulku 2011; Englert & Rubio, 2005;

Weatherley & Miladinovic, 2004; Demir et al, 2002). Cation exchange capacity (CEC) of zeolite depends on nature of the cation (example: size, load), structural characteristic of zeolite, and concentration of cations in the solutions (Sarioglu, 2005). When using IE as NH_3 removal method, a lab scale testing is necessary as it allows examination of influential parameters such as particle size, pH, contact time, loading effects, and flow rate on zeolites performance. Although many researches have been studying these parameters (Huang et al, 2010; Du et al, 2005; Wen et al, 2006), zeolites from different regions have its own special characteristics and require individual research.

The aim of this study is to investigate NH_3 removal from wastewater using zeolite supplied by Zeocom[®], Slovak Republic. The experiments were conducted in two phases: batch and column studies. The batch method was used to study the effect of pH, initial NH_4^+ concentration, contact time, kinetics, and equilibrium isotherms on zeolite N-removal efficiency. Similarly, column studies were carried out to determine the effect of flow rate, pH, and regeneration capacity of the zeolite. In addition, batch studies were carried out to ascertain the effect of total solids (TS) on zeolites performance.

2. OBJECTIVE

The aim of this thesis work is to study NH_3 removal from wastewater and bioslurries using natural sorbent material (zeolite) and cation exchange method. Furthermore, regeneration capacity of exhausted zeolite was studied using chemical regeneration: sodium chloride (NaCl), and hydrochloric acid (HCl). NH_3 removal efficiency (E%) was studied in two phases: batch and column methods. NH_3 removal is influenced by different parameters such as grain size, pH, NH_4^+ concentration, and flow rate. In this study, we used two grain sizes that are 0.2-0.5 mm and 0.6-2.0 mm for both batch and continuous methods.

In the batch experiments, the focus was to test the effect of grain size, pH, and various initial NH_4^+ concentrations on the zeolite E% within a given time frame. The batch experiments were carried out to study kinetics and equilibrium isotherm to determine the suitability of the process. Additionally, the effect of TS ratio on NH_3 removal at constant load was studied using batch experiment.

The column method gives insight into how will zeolites performs in natural environment. In column method, the experiments mainly focused on studying the effect of grain size, pH, and flow rate on NH_3 E% at constant NH_3 load.

Regeneration capacity was studied using the column method. Chemical regeneration was carried out to test the effectiveness of NaCl and HCl at different concentration and the effect of multiple regenerations on the IE capacity of the zeolites.

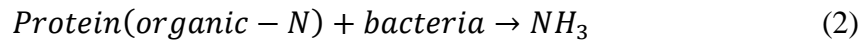
3. LITERATURE REVIEW

Wastewater produced from industries, agriculture, and municipalities contains large amount of ionic pollutants. These ionic pollutants can be replaced with desirable ions using IE before discharging wastewater into natural systems.

3.1 Nitrogen Cycle

Nitrogen (N) is an essential nutrient for all organisms. It is a key component of all proteins and enzymes (El-Hady et al, 2001). N is abundant in earth's atmosphere but cannot be used directly by biological systems. In order to use N by plants, and animals, reactive N forms are needed. Therefore, atmospheric N is changed into reactive forms through biological, chemical, and photochemical processes. Reactive N occurs in various forms that is nitrous oxide (N₂O), nitric oxide (NO), ON, NO₂⁻, NO₃⁻ or NH₃ (Franus & Wdowin, 2010; Farkas et. al. 2005). It naturally cycles through the biosphere as shown in Figure 1. The N cycle consists of five processes: nitrogen fixation, nitrification, denitrification, mineralization, and immobilization. The first three processes are important for water systems (U.S.EPA, 2013).

N fixation is a process where dinitrogen (N₂) is reduced to NH₃. It can be carried out by biological (equation 2) or chemical processes (equation 1). In the N fixation process, triple bond of N₂ is broken down, which requires substantial amount of energy and three atoms of hydrogen (H₂). Similarly, biological N fixation in natural system is carried out by symbiotic bacterium such as *Rhizobium*, *Casuarina*, *Alnus* and cyanobacteria. [Madigan et al, 2012].



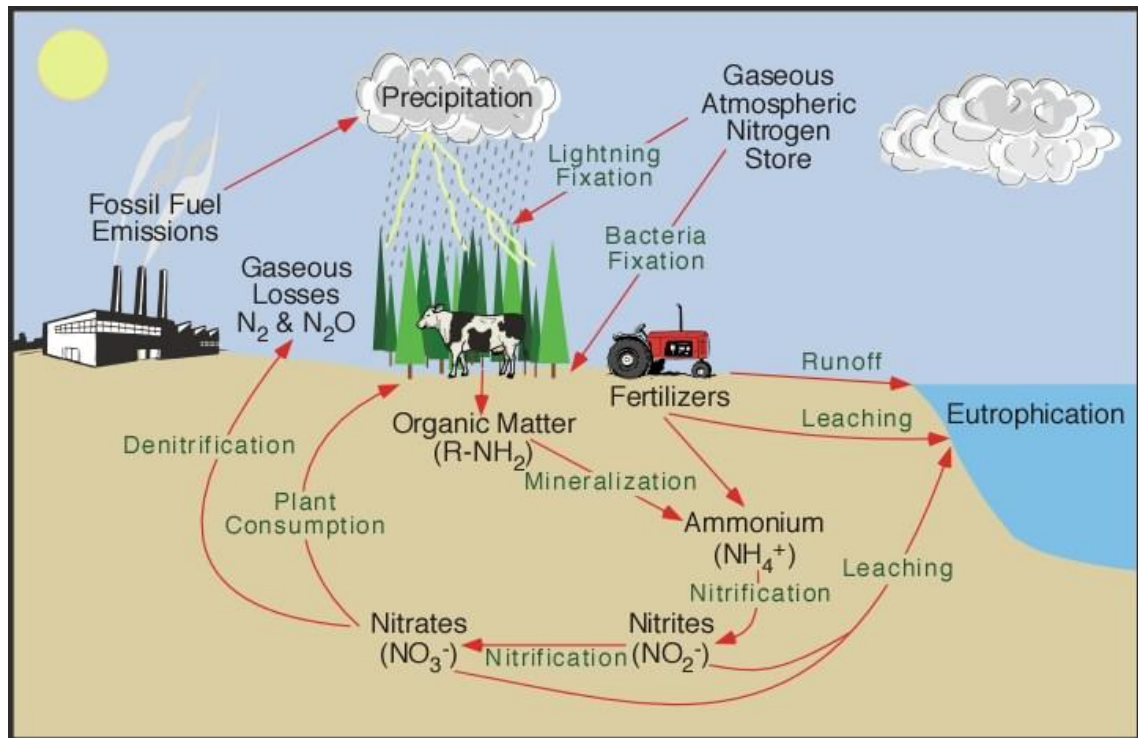
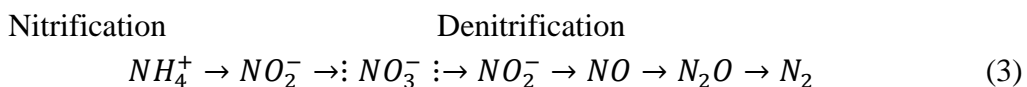


Figure 1: The nitrogen cycle (Pidwirny, 2006).

NH_3 and NO_2^- are oxidized into NO_3^- by nitrifying bacteria in the nitrification process. Nitrifying bacteria are abundant in soil and water and nitrification is usually carried out by two groups of nitrifying bacteria. One group (example: *Nitrosomonas*) oxidizes NH_3 to NO_2^- , and another group (example: *Nitrobacter* and *Nitrospira*) oxidizes NO_2^- to NO_3^- . NO_3^- formed during nitrification process is reduced into N_2 under anoxic condition in the denitrification process. Denitrification step is carried out by heterotrophic bacteria (example: *Pseudomonas*, *Achromobacter*, *Micrococcus*) which converts NO_3^- into NO , N_2O and finally into N_2 under anoxic condition. The nitrification and denitrification process is shown in equation 3. [Ruiz et al, 2006; Madigan et al, 2012].



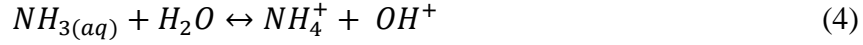
3.2 Ammonia

NH_3 is produced during decomposition of organic waste matter, gas exchange with the atmosphere, forest fires, animal waste, nitrogen fixation, industrial emission, release of fertilizers, and discharge of NH_3 by biota in the environment. Industrially, NH_3 is produced by the Haber process where N_2 is converted to NH_3 using H_2 obtained from natural gas (methane) under high pressure, and heat (equation 1). NH_3 has many applications in agriculture as well as in industries. It is used in agriculture directly as fertilizer or precursor for many other N based fertilizers. In industries, it is used for numerous applications such as in mining industry for metal extraction, petroleum

industry for processing of crude oil, and in corrosion protection. It is also used for production of dye and pharmaceutical products. [U.S.EPA, 2013].

NH_3 enters water bodies via agricultural runoff, nitrogen fixation, excretion of nitrogenous wastes from animals and wastewater discharges from municipalities and industries. In 2011 in the US, approximately 4.7 million pounds (2.13 million kg) of NH_3 was discharged into fresh water from industries alone (U.S.EPA, 2013; U.S. EPA 2011). Hence, NH_3 discharged from municipal, industries, and agricultural wastewater resources must be removed or recovered before it reaches receiving water bodies.

In water, NH_3 is either present in non-ionized ammonia ($\text{NH}_{3(\text{aq})}$) or ionized ammonium (NH_4^+) depending on pH and temperature (Franus & Wdowin, 2010; Miladinovic et al, 2004; Thornton et al, 2007; Körner et al, 2001). $\text{NH}_{3(\text{aq})}$ acts as a weak base, and NH_4^+ as a weak acid. $\text{NH}_{3(\text{aq})}$ and NH_4^+ are interrelated through the chemical equilibrium as shown in equation 4 (Maranon et al, 2006) and equation 5 (Leyva-Ramos et al 2004; Leyva-Ramos et al, 2010)



$\text{NH}_{3(\text{aq})}$ and NH_4^+ distribution in water over a range of pH at 25°C is shown in Figure 2. From Figure 2, it is clear that NH_3 is present as NH_4^+ ion at pH below 7, and as $\text{NH}_{3(\text{aq})}$ at pH greater than 11.5. Similarly at about pH 9.25, $\text{NH}_{3(\text{aq})}$, and NH_4^+ concentration is equal. The concentration of NH_4^+ decreases with increase in pH and transformed into $\text{NH}_{3(\text{aq})}$, and vice versa. In fresh water, the ratio of $\text{NH}_{3(\text{aq})}$ to NH_4^+ increases by 10-fold at a single unit rise of pH (U.S. EPA, 2013).

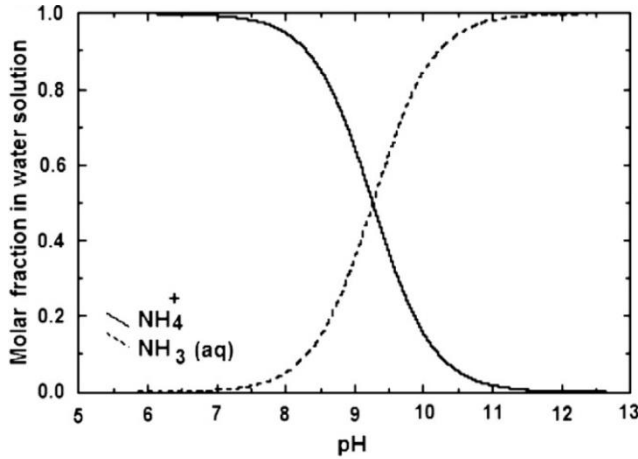


Figure 2: Diagrammatic representation of ammonia behavior in water solution at $T = 25^\circ\text{C}$ (Leyva-Ramos et al, 2004; Widiastuti et al, 2011).

The amount of NH_3 in a solution can be calculated using equation 6 (Maranon et al, 2006):

$$\text{NH}_3 = \frac{17}{14} \times \frac{N - \text{NH}_4^+ \times 10^{\text{pH}}}{\frac{K_b}{K_w} + 10^{\text{pH}}} \quad (6)$$

Where, K_b is NH_4^+ ionization equilibrium constant, and K_w is the ionization constant of water. K_b , and K_w can be calculated as shown in equation 7, and 8 (WHO, 2003).

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \text{ at } 25^\circ\text{C} \quad (7)$$

When the acid-base is at equilibrium

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.10^{-14} \quad (8)$$

Since, the relative concentrations of NH_3 and NH_4^+ are pH and temperature dependent, K_a can also be calculated by using equations 9 & 10 (Körner et al, 2001):

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = 5.7 \times 10^{-10} \quad (9)$$

$$pK_a = \frac{0.09108 + 2729.92}{(273.2 + T)} \quad (10)$$

The concentration of free NH_3 can be calculated using equation 11 when total NH_3 concentration is known (CRC handbook of chemistry and physics, 1977).

$$\frac{\text{NH}_3}{\text{TNH}_3} = (1 + 10^{pK_a})^{-1} \quad (11)$$

Where, NH_3 and TNH_3 is free and total NH_3 concentration (mg/l), respectively, K_a is ionization constant of TNH_3 (moles/l).

Using pH, and temperature of the solution, $\text{NH}_{3(\text{aq})}$ fraction can be calculated using equation 12 (Körner et al, 2001)

$$\text{NH}_3(\%) = \frac{100}{(1 + 10^{(pK_a - pH)})} \quad (12)$$

3.3 Problems caused by NH_3 in water

The continuous increase of NH_3 and nitrogenous compound in water system has become a major water problem in current time. NH_3 is an indicator for recent water pollution (Brinzei et al, 2005) and is present at concentration of 12 mg/l and less than 0.2 mg/l respectively in fresh water and ground water under natural conditions (WHO, 2003). However, NH_3 is present in high quantities in municipal, agricultural, and industrial wastewater such as distilleries, fertilizer plants, paper manufacturing plants, oil refineries, and slaughterhouse (Miladinovic et al, 2004; Penn et al, 2010). Excess NH_3 in water can lead to various problems such as reduction in disinfection efficiency, taste, and odor problems (Bedeleian et al, 2010), corrosion/biological fouling problem in industrial water system (Widiastuti et al, 2011; Englert & Rubio, 2005), decrease in dissolved oxygen level (Erdogan & Ulku, 2011), and eutrophication problem in rivers, lakes, coastal seas and estuaries (Franus & Wdowin, 2010). NH_3 is also toxic to fish and other aquatic animals. When NH_3 is present at high concentration in water, aquatic organisms are unable to excrete toxicant which leads to toxic buildup in internal tissues and blood, and probably death (EPA, 2013).

3.3.1 Disinfection, taste, and odor problem

NH_3 can interfere with chlorine (Cl) disinfection process by forming monochloramine (NH_2Cl), dichloramine (NHCl_2) and trichloramine (NCl_3) making Cl unavailable for disinfection as shown in equations 13, 14, & 15. When drinking water containing more than 0.2 mg/l NH_3 is chlorinated, approximately 68% Cl reacts with NH_3 and becomes unavailable for disinfection. This leads to reduction in disinfection efficiency and causes taste and odor problems. World Health Organization (WHO) suggests that NH_3 concentration above 1.5 mg/l can cause taste and odor problems in water. [WHO, 2003; EPB 431, 2012].



3.3.2 Eutrophication and reduction in dissolved oxygen level

Eutrophication occurs naturally depending on the local geology and natural feature of the catchment areas of lakes, reservoirs, rivers, and coastal oceans. But human activities have accelerated the eutrophication process, which is referred to as cultural eutrophication. Cultural eutrophication is a serious problem affecting ecosystems from the Arctic to the Antarctic (Smith et al, 2009). Cultural eutrophication is caused by excessive inputs of nutrients (P and N) into water resources, and marked by algae bloom, depletion of O_2 , deterioration of water quality, and fish kills. Eutrophication has many adverse effects on marine and fresh water ecosystem, which is listed in Table 1.

Table 1: Effect of eutrophication

Decrease in oxygen concentration	Gray et al, 2002; Smith et al, 2009; Smith et al, 1999; Bonsdorff et al, 1997
Increase in organic matter production and sedimentation	Gray et al, 2002; Bonsdorff et al, 1997
Destruction of habitat for fish and shellfish	Anderson et al, 2002
Increased turbidity and reduced transparency of the water	Anderson et al, 2002; Bonsdorff et al, 1997; Smith et al, 2009; Smith et al, 1999
Increase in algae biomass	Anderson et al, 2002; Smith et al, 2009; Smith et al, 1999
Reduction in species diversity	Smith et al, 2009; Smith et al, 1999
Decrease in aesthetic value of the water body	Smith et al, 2009; Smith et al, 1999

Aquatic plants need N and P in small amount for growth, but, in large amount causes rapid growth of algae. The excessive algal bloom affects water system by blocking sunlight and using oxygen present in water. When algae bloom block sunlight from penetrating inside water, it affects submarine photosynthetic activities causing

death of plants in this region. In addition, when plant and blooms die, they decompose by bacteria, consuming oxygen from water system. This will lead to depletion of dissolved oxygen level, which will eventually kill fish and invertebrates in water due to hypoxia or anoxia. Eutrophication process is represented in Figure 3.

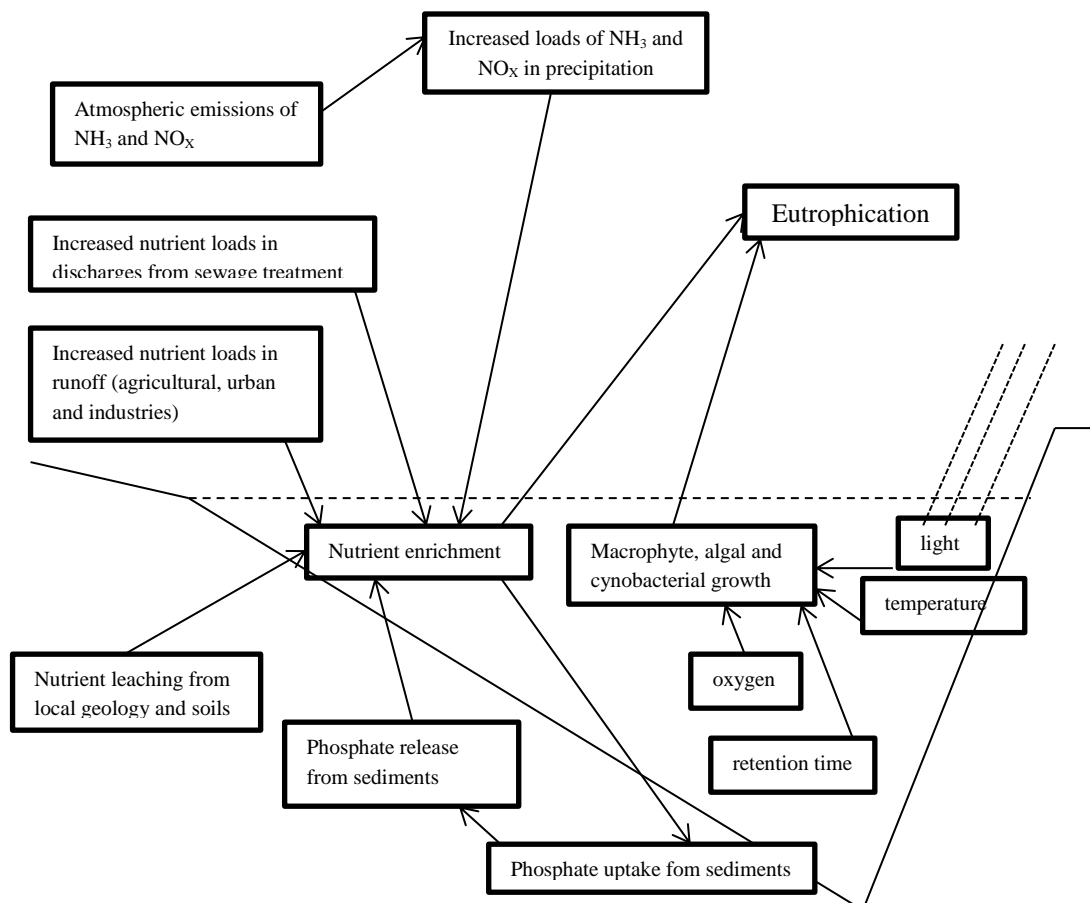


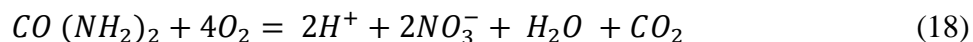
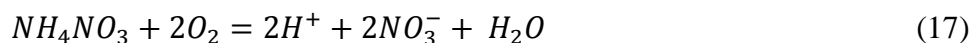
Figure 3: Schematic illustration of eutrophication process (adapted from National Eutrophication Monitoring Programme Implementation, 2002)

3.3.3 Soil acidification

Soil acidification is continuously increasing as a result of continuous cropping and use of fertilizers. It affects soil biology by reducing pH, fertility, and buffering capacity of the soil (Wang et al, 2010). When pH of the soil is below 5.5, breakdown of organic matter is reduced which results in nutrient loss from organic matter. This phenomenon has negative impact on organism living in soil such as bacteria, fungi, and earthworm (VitiNotes, 2006).

The continuous use of NH_3 based fertilizers can cause soil acidification. When NH_3 is applied in the soil, it binds to water, soil or organic matter, which is converted into NO_3^- by bacteria in the soil. In the process, hydrogen (H^+) ion is released into the soil. The excess accumulation of H^+ ion in soil causes soil acidification. The most important acids forming reaction to fertilizer by microbial action are nitrification of NH_3 and

ammonical nitrate (NH_4NO_3), hydrolysis of urea ($\text{CO}(\text{NH}_2)_2$), and nitrification of products as shown in equations 16, 17, and 18 (Barak, 1997).



When acidified leaching water enters water bodies, it acidifies water resources and affects aquatic life, ground and drinking water supply.

3.3.4 NH_3 effect on human health

NH_3 effects in human are restricted to sites of direct contact like skin, eyes, mouth, and respiratory and digestive track. Acute health effects of NH_3 are eyes, nose, throat, and skin irritation and burns. Similarly, chronic effects of exposure to high doses of concentrated NH_3 can cause permanent blindness, lung disease or death. [ATSDR, 2004].

NH_3 is dangerous to infants and can cause blue baby syndrome. When NH_3 reacts with Cl , it forms NH_2Cl (equation 13) and NH_2Cl increases the concentration of NO_3^- in water. Blue baby syndrome is usually caused by NO_3^- ingestion, where infants develop blue-grey or lavender skin color. NO_3^- oxidizes iron (Fe) in hemoglobin (Fe^{2+}) to methemoglobin (Fe^{3+}). Fe^{3+} destroys ability of red blood cell to transport oxygen. Infants in their first 6 months are susceptible to blue syndrome because infants have low amount of red blood cell enzyme (methemoglobin reductase) which converts Fe^{3+} to Fe^{2+} . Fe^{3+} greater than 50% can lead to coma and death. [Knobeloch et al, 2000].

3.3.5 NH_3 and NH_4^+ effect on aquatic animals

NH_3 is very toxic to all the vertebrates in aquatic system causing lethal problems such as coma, convulsions, and death. The death of vertebrates is caused by potassium (K^+) displacement with increase in NH_4^+ concentration which tends to depolarizes neurons causing cell death in the central nervous system. [Franus & Wdowin, 2010; Randall & Tsui, 2002].

NH_3 is very toxic to fish even at low concentration. It has negative effects on fish tissues and physiological factors such as growth rate, oxygen consumption, and disease resistance (Asgharinghadan et al, 2012). Most biological membranes are permeable to NH_3 but considerably less permeable to NH_4^+ ions (Randall & Tsui, 2002). Therefore, NH_3 is more toxic to fish, and NH_3 toxicity increases with rise in water pH. The maximum uptake of NH_3 is about 2 mg/L at a temperature of 18°C and pH 5-7 (Celik et al, 2001).

3.4 European Union and Finnish laws on NH₃ in the environment

In order to prevent and protect both aquatic and terrestrial organisms and ecosystem as a whole, discharge of wastewater into water resources should be monitored and controlled. The guided level for NH₃ release into water bodies is different in various part of the world. For example, The Council of European Union (EU) for drinking water has set the guide level of NH₃ in drinking water at 0.05 mg/L and maximum limit of 0.5 mg/L (Celik et al, 2001; Siljeg et al, 2010). Similarly, The Environmental Protection Agency (EPA) and the American Committee on Water Quality Criteria have suggested a value below 0.02 mg/l N-NH₃ (Miladinovic & Weatherley, 2008).

EU adopted Water Framework Directive (WFD) in 2000 to protect and ensure the water qualities in member countries. It aims to prevent ground and surface water pollution, and manage water in sustainable ways. The EU understands the need for water for health, sustainable economic growth, and prosperity of the society. Therefore, it aims to ensure that all water resources meet “good status” by 2015. [EU, 2010].

Water is the core of natural ecosystem and climate change. EU has introduced legislation to control and monitor water bodies. The Directive 76/464/EEC is one among them and it addresses the problem with chemical substances introduced into water. In it, NH₃ is listed in list II, which includes chemical substances having deleterious effect on the aquatic environment. The recent studies showed 20% of all surface water in the EU is seriously threatened with pollution. Approximately 40% of European lakes and rivers show signs of eutrophication. [EU, 2010].

To meet EU goals of "good status" of water resources by 2015, Finland has implemented many programs. Finnish Environmental Institute checks status of water all over Finland at regional scale every year. Finland has numerous lakes and rivers of which 85% of the lakes and 65% rivers are in good or very good state. However, three quarters of surface area of coastal water and small lakes suffer from eutrophication. The shallowness and ice covered Finnish lakes (average depth approximately 7 meters) and the Baltic Sea (mean depths of 55 meters) are more vulnerable to pollution. It is because in cold conditions harmful substances degrade slowly, and ice cover winter prevents oxygen being transferred from air to surface water. [SYKE, 2013]

Eutrophication is major problem in the Baltic Sea. More than a century long deposition of nutrients in the Baltic Sea has caused surface accumulation of phytoplankton which has resulted in decreased visibility and biodegradation of organic sediment (e.g., algae is contributing in creation of anoxic bottom). Finland deposits approximately 74000 metric tons of N in the Baltic Sea of which natural runoff account to 38%, agriculture (27%), and total nitrogen originated from wastewater (15%).[http://www.itameriportaali.fi/en/tietoa/rehevoityminen/en_GB/rehevoityminen_itameri/].

Finland adopted programs to protect the Baltic Sea in 2000. Finland along with other countries sharing the Baltic Sea Coast established, “The Baltic Marine

Environment Protection Commission”, also known as HELCOM in 1974 to protect marine environment in the Baltic Sea. HELCOM is an intergovernmental organization of the nine Baltic Sea coastal countries and the EU. In 2013 HELCOM Ministry meeting was mainly focused on work to reduce nutrient inputs which cause eutrophication in the sea. [HELCOM, 2013].

The increased awareness about harmful effects of NH_3 and stringent laws restricting discharge of NH_3 has made it compulsory for the removal of NH_3 from municipal and industrial wastewater in the EU nations.

4. ION EXCHANGE

IE is a common phenomenon in nature. It is a reversible chemical reaction which takes place between two phases either solid-gas or liquid-solid systems. In this process, ions from a solution are replaced by an equivalent amount of free mobile ions of similar charge from the ion exchanger. IE process is stoichiometric process where electroneutrality has to be maintained all time. Therefore, every ion removed from the framework should be replaced by another ion of the same charge from the solution. Figure 4 shows a simple example of IE. In Figure 4(a) potassium (K^+) ions in the solution are exchanged with sodium (Na^+) ions in the exchange material. Similar phenomenon is shown in Figure 4 (b) and Figure 4(c) with different ions sequence.

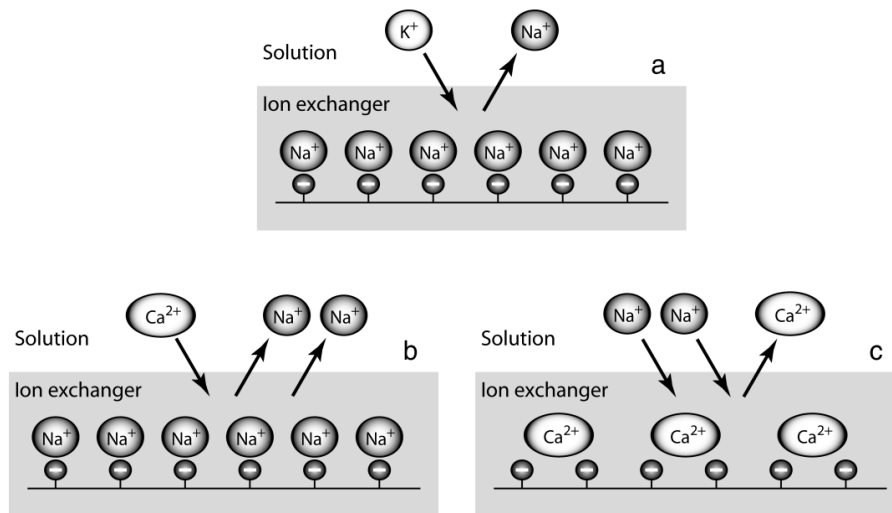
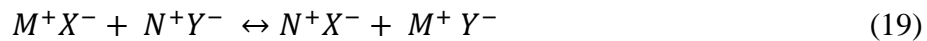


Figure 4: Ion exchange (Zagorodni, 2007)

Ion exchange in equilibrium can be represented as (Kumar & Jain, 2013):



In equation 19, M^+X^- is ion exchanger where M^+ is mobile free ion and X^- is the fixed ion in exchanger. N^+Y^- is ions in the solution. When the solution is passed through the M^+X^- ion exchanger, the solution will ionize into N^+ and Y^- ions. M^+ free mobile ions in ion exchanger will be exchanged with similar charged N^+ ions in the solution. Steps involved in ion exchange are illustrated in Figure 5.

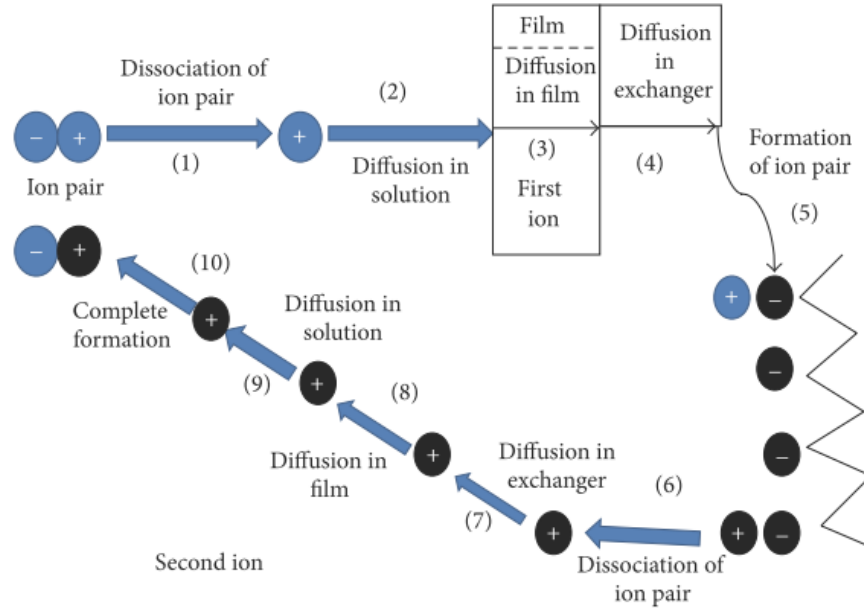
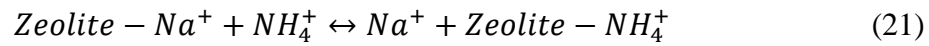


Figure 5: Steps involved in ion exchange process (Kumar & Jain, 2013).

In the case of zeolites, IE process between cations in solution $Z_B B_{Z_A}^{Z_A+}$ and cations in zeolite framework $Z_A B_{L_{Z_B}}$ can be represent as in equation 20 (Wang & Peng, 2010; Harjula 1993).



Where Z_A^{+} and Z_B^{+} are valances of respective cations and L is the portion of zeolite holding unit negative charge. For case of NH_4^{+} exchange by zeolite, NH_4^{+} ions in solution is exchanged with the same charged ions (e.g., Na^{+}) in a zeolite framework as shown in equation 21.



IE as a phenomenon was discovered more than 100 years ago. But around 1850s, two agricultural chemists, Thompson and Way discovered that certain soils had greater ability to absorb NH_3 compared with others (Kumar & Jain, 2013; Nasef & Ujang, 2012). In 1910, cation exchanger (natural zeolite) was used to soften water (DOW, 2000). IE methods using various exchangers have been studied in depth by many researchers (Cyrus & Reddy, 2011; Franus & Wdowin, 2010; Sarioglu, M., 2005).

4.1 Ion exchange materials

IE materials are backbone of any IE process. Ion exchangers are insoluble substances with open structure, which contain fixed and mobile ions. It is porous in nature and contains water inside the beads. The fixed ions are permanent part of the framework and neutralized by loosely held counter ions. These counter ions move throughout the framework and can be exchanged with similar charge ions in solutions. IE materials are available in different forms and structures. [Alexandratos, 2009]. These materials are classified into different categories depending upon its origin, and ionic group (Figure 6).

4.1.1 On the basis of ionic groups

IE materials are classified into two categories based on ionic group attached to the exchange materials that is cation exchanger and anion exchangers. When negatively charged groups (e.g., sulphate (SO_4^{2-}), carboxylate (RCOO^-), phosphate (PO_4^{3-}) and benzoate) are fixed ions and allow the passage of positively charged ions, it is called cation exchanger. Similarly when positively charged groups (e.g., amino group, alkyl substituted phosphine, and alkyl substituted sulphides) are fixed ions and allow passage of negatively charged ions, it is called anion exchanger. [Kumar & Jain, 2013].

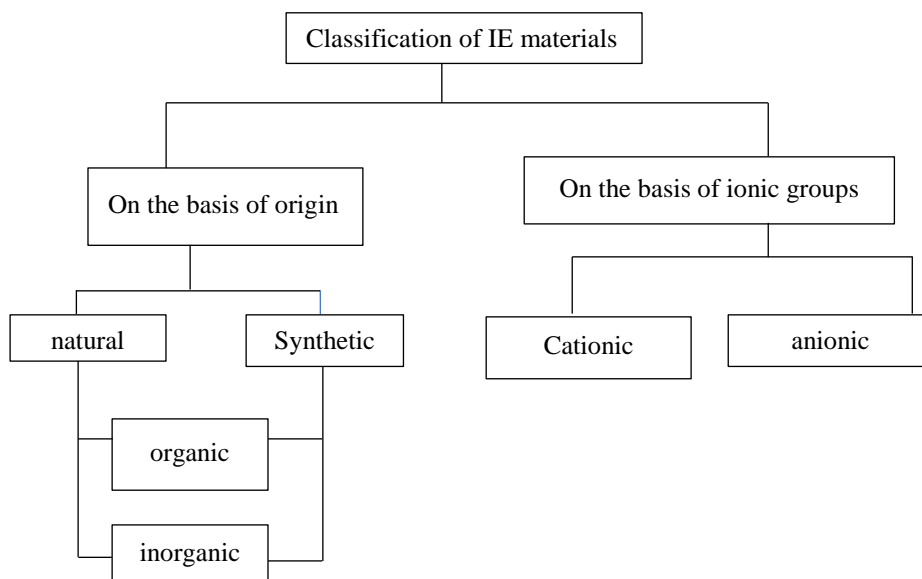


Figure 6: Classification of ion exchange materials

4.1.2 On the basis of origin

On the basis of origin IE materials can be classified as natural and synthetic exchanger. Natural ion exchanger is abundant in nature and easily available. It can be further classified as organic and inorganic (minerallic) exchanger.

4.1.2.1 Organic ion exchange materials

Proteins (casein, keratin and collagen), polysaccharides (cellulose, straw, and peat) and carbonaceous materials (charcoals, lignites, and coals) exhibit IE properties. Organic exchanger can be cationic, anionic and amphoteric (cationic/anionic) exchanger depending on function group (or nature of fixed ion). Carboxyl groups ($-\text{COOH}$), and phenolic groups present in animal and plant cell are weakly acidic in nature and acts as ion exchanger under neutral and alkaline conditions. [Kumar & Jain, 2013]. An example of IE in organic exchanger is shown in Figure 7 where H^+ ion from COOH group is exchanged with Na^+ or copper (Cu^{2+}) cations.

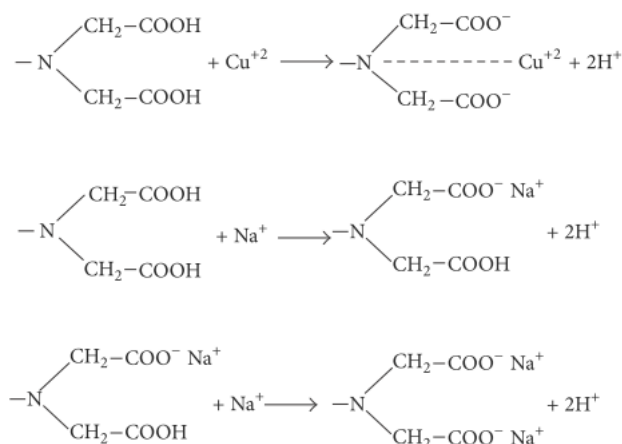


Figure 7: Functional group (COOH) as ion exchanger in nature (Kumar & Jain, 2013).

4.1.2.2 Inorganic ion exchange materials

Natural inorganic materials such as clays (bentonite and kaolinite), vermiculite, and zeolites exhibit IE properties (IAEA, 2002; Kumar & Jain, 2013). The inorganic exchanger can exist only in cation exchange form (Nasef & Ujang, 2012). The physiochemical properties, mechanical stability, and high specific surface make it efficient adsorbent for wastewater treatment (Bourliva et al, 2010). Inorganic IE materials are discussed in detail in Section 5.

4.1.3 Modified natural ion exchange materials

To overcome the drawbacks of natural IE, they are modified to improve exchange capacity and selectivity. For example: cellulose based ion exchangers can be modified by introducing PO_4^{3-} , carbonic or other acidic functional group. The sorption parameter of inorganic natural ion exchanger can be modified by chemical or thermal treatment (Kumar & Jain, 2013). For example: pretreatment of zeolite with NaCl will transform zeolite into homoionic form. This treatment substitute the exchangeable cations (K^+ , Ca^{2+} , and Mg^{2+}) with Na^+ cations.

4.1.4 Synthetic ion exchange materials

Synthetic ion exchangers are produced by tailoring chemical compounds with desired physical and chemical properties. They are produced either by polycondensation or polymerization. They are composed of a matrix, three dimensional high molecular network with charged functional groups attached to it. The nature of the ion exchanger is determined by charge of the group attached to the resin matrix. [Kammerer et al, 2011]. For example, synthetic organic ion exchanger, Bakelite can be prepared by heating phenols and formaldehyde in presence of acid or base as shown in Figure 8 (Kumar & Jain, 2013). Synthesized IE matrix have higher exchange capacity, chemical

and mechanical stability, uniform in particle size compared with a natural one (Farkas et al, 2005, Kumar & Jain, 2013).

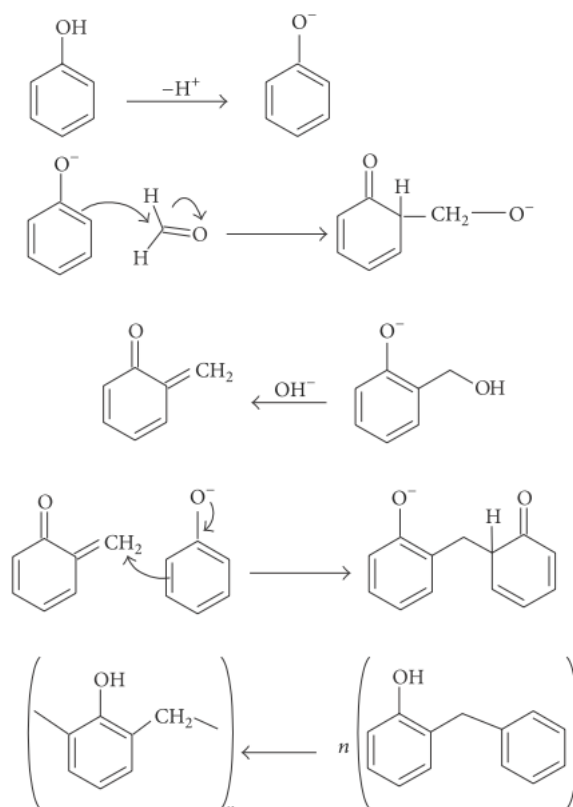


Figure 8: Mechanism for synthesis of Bakelite (Kumar & Jain, 2013).

4.2 Ion exchange and adsorption

Adsorption is the process in which molecules from solution accumulate in the internal or external surface of the porous solid. Adsorption occurs either by physisorption or chemisorption. Physisorption is the weak interaction between adsorbed molecule and solid surface due to van der Waals force and chemisorption is the interaction due to strong ionic or covalent bonding. [Gupta & Suhas, 2009; Kammerer et al, 2011]. The difference between physisorption and chemisorption is presented in Table 2.

IE and adsorption process shares some basic characteristics. The most common step in both the processes is mass transfer of molecules from the aqueous to the solid phase. Since, IE and adsorption are both diffusion processes, they are grouped together for a unified treatment and called as sorption process [Inglezakis & Pouloupoulos, 2006; Gupta and Suhas, 2009]. Sorption consists of four steps which are as follow (Edrogon & Ulku, 2011):

- i. Transfer of ions from the bulk solution to external layer of the sorbent
- ii. Diffusion of ions across the liquid film surrounding the particle.
- iii. Diffusion of ions in the pores and surface
- iv. Sorption of ions into active site

Table 2: Difference between physiosorption and chemisorption (adapted from Ruthven, 1984)

	Physiosorption	Chemisorption	References
Electron exchange	no	yes	Ruthven, 1984; Inglezakis & Pouloupoulos, 2006
Saturation uptake	Multilayer	Monolayer	Ruthven, 1984; Inglezakis & Pouloupoulos, 2006; Mulero et al, 2006; Proykova, 2006
Degree of specificity	low	High	Ruthven, 1984; Verma et al, 2008
Heat of adsorption	Low	High	Ruthven, 1984; Verma et al, 2008
Adsorption enthalpy	exothermic	endothermic or exothermic	Ruthven, 1984; Mulero et al, 2006
Nature of adsorption	Rapid, non-activated, reversible	Activated, may be slow and irreversible	Ruthven, 1984; Inglezakis & Pouloupoulos, 2006; Verma et al, 2008; Proykova, 2006

4.3 Application of ion exchange

IE method is a well-developed and effective method. The advantage of IE method is small space and simple in application and operation (Du et al, 2005; Widiastuti et al, 2011; Huo et al, 2012). It is relatively low cost technology (Widiastuti et al, 2011) and can be operated at wider range of temperature. It also has ability to handle shock loading (Cyrus & Reddy, 2011). Its applications are listed in Table 3. The major IE applications in water treatment system are discussed in this section.

Table 3: Application of ion exchange methods

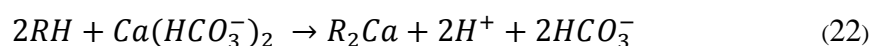
Treatment of drinking water (water softening, and demineralization)	Bochenek et al, 2011
Production of acids, bases, and salts	Bochenek et al, 2011
Industrial drying and treatment of gases	Bochenek et al, 2011
Wastewater decontamination (removal of ammonia, heavy metals, and organic pollutants)	Bochenek et al, 2011; Brinzei et al, 2005; Curkovic et al, 1997; Cyrus and Reddy, 2011; Cincotti, et al, 2001
Recovery of metals	Cincotti et al, 2001; Villiers, et al, 1997
Removal and purification of radioactive isotopes	Curkovic et al, 1997
Energy production	Cincotti et al, 2001
Food industry	Bochenek et al, 2011
Biomolecular separation	Bochenek et al, 2011

4.3.1 Water softening

Hard water forms scale deposits in water using appliances such as pipes, boiler, dishwasher, and solar heating system. Scale deposits reduce efficiency and damage the appliances. Hardness in water is caused by presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions and can be removed by exchanging Ca^{2+} and Mg^{2+} ions with cations such as Na^+ or K^+ ions. For example, Na-zeolite softening is commonly used in steam boilers and industrial water treatment applications (Skipton et al, 2008).

4.3.2 Dealkalisation

Dealkalisation is a process to remove temporary hardness in water, which is usually caused by bicarbonates (HCO_3^-). The raw water is passed through weak H^+ cation exchange resin. In this process, resin removes Ca^{2+} and Mg^{2+} ions and bicarbonate ion is present as a solution of carbon dioxide and water in outlet effluent (equation 22 & 24). The carbon dioxide in solution is removed by passing water through degasser column (Figure 9). [Aqua Chem, 2013].



Dealkalisation is usually applied in breweries, household drinking water filters, and low pressure boiler. It also removes the salinity of water.

4.3.3 Demineralisation

Demineralization is a process where dissolved salts and minerals from water are removed. It is also known as deionization. IE was the first method used to obtain demineralized water (DOW, 2000). Demineralized water is used in many applications such as wastewater treatment, power generation, petrochemicals, steel manufacture, food and beverage, electronics, pharmaceuticals, metal finishing, and paper manufacture (OVIVO, 2012).

Wastewater influent contains numerous contaminants. The simplified demineralization process for wastewater is shown in Figure 9. In Figure 9, first the influent is passed through a cation exchange resin where cations are replaced with equivalent amount of H^+ ion. The resultant acidic solution is passed through another anion exchange resin where anions present in wastewater are substituted with equivalent amount of OH^- ions. When the cation and anion beds are exhausted, they are regenerated with HCl and NaOH respectively.[WasteWater System, 2013].

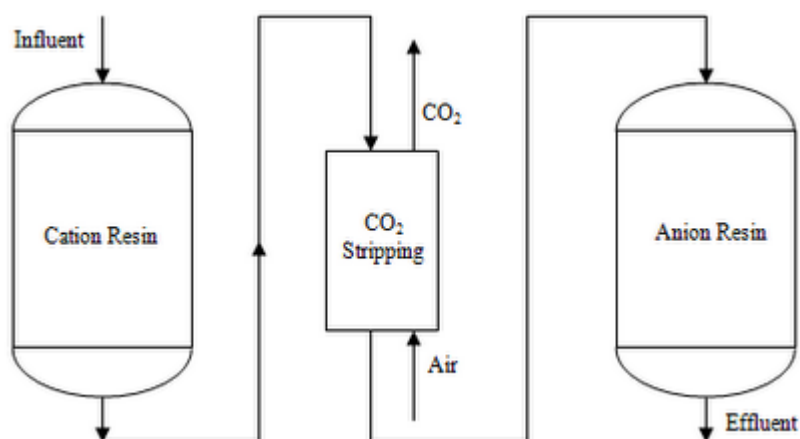


Figure 9: Diagrammatic representation of demineralization of wastewater (WasteWater System, 2013).

4.3.4 Heavy metal removal

Heavy metals should be removed from wastewater treatment system before release into the environment. It is because of potential accumulation and toxicity of these metals. IE is one of the most commonly used treatment processes for heavy metal removal (Cincotti, et al, 2001; Curkovic et al, 1997). Natural and synthetic materials have been used to remove metal from the wastewater. Natural material such as zeolite have high selective for heavy metal such as lead (Pb), zinc (Zn), Cu and cadmium (Cd). Hence, zeolite can be used to remove heavy metals from waste system. However, zeolite is selective to number of ions and presence of other ions increases competition for adsorption sites. Similarly, synthetic materials with higher selectivity for desired metals can be implemented. The economic feasibility of IE can be increased by removing and recovering valuable metals.

5. ZEOLITE

Zeolites are natural minerals found worldwide, discovered in 1756 by a Swedish mineralogist, A.F. Cronstedt (Payra & Dutta, 2003). The word “zeolite” is derived from Greek words: “Zeo” means “to boil” and “lithos” means “stone” (Maesen & Marcus, 2001). Natural zeolites were formed thousand million years ago as a result of chemical reactions between volcanic ash and alkaline water (Bogdanov et al, 2009).

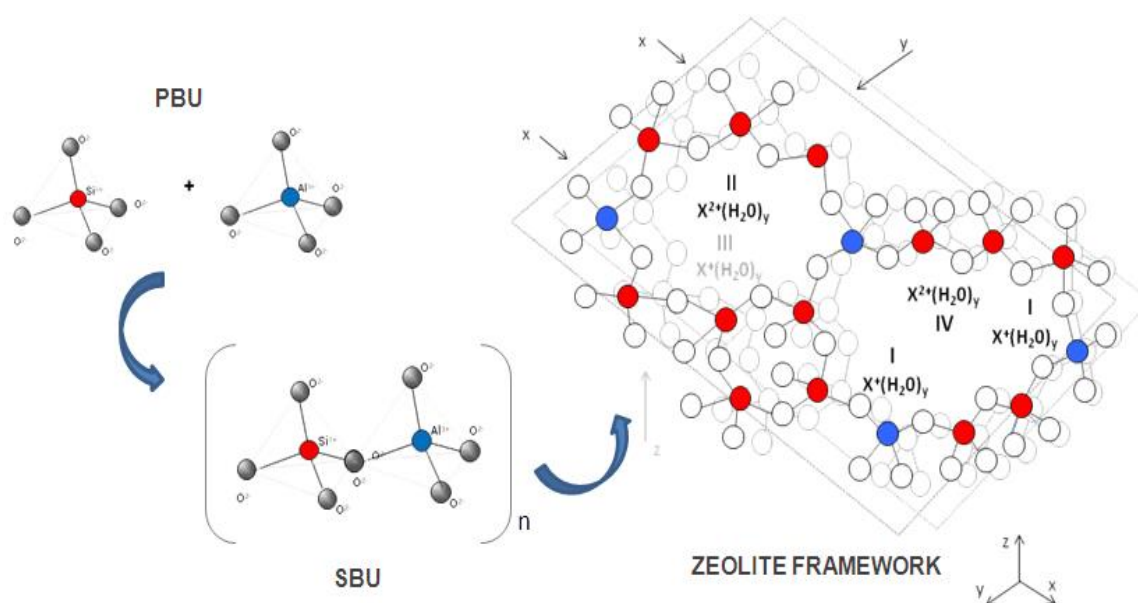


Figure 10: Simplified 3D structure of zeolite (Margeta et al, 2013)

Zeolites are crystalline, micro-porous, hydrated aluminosilicate (Al_2SiO_5) minerals of alkali and alkaline earth metals and its composition is generally represented as $\text{M}_{y/z}[(\text{SiO}_2)_x(\text{AlO}_2)_y]n\text{H}_2\text{O}$, where M is an exchangeable cation with a valence z (Harjula, 1993). Zeolite is structurally composed of Al_2SiO_5 framework, exchangeable cations and zeolitic water. The Al_2SiO_5 framework is most stable and conserved component and defines the structural type of zeolite. The Al_2SiO_5 framework is tetrahedron in structure. The center of this structure is occupied by silicon (Si) or aluminum (Al) atom with four oxygen atoms at the corners (Figure 10). The substitution of Si^{4+} by Al^{3+} ions produces negative charge in the framework and this charge is balanced by exchangeable monovalent (e.g., Na^+ , K^+) or divalent (e.g., Ca^{2+} , Mg^{2+}) cations (Wang et al, 2007; Wang & Peng, 2010; Zhao et al, 2010). Each Al^{3+} atom substitution for Si^{4+} atom generates one negative charge to frame work which means higher the amount of Al^{3+} atoms higher the negative charge of the zeolites (Widiastuti et al, 2011). Hence, large numbers of cations needed to balance negative charges. The compensating cations are reversibly fixed by interactions and can be easily changed

with other cations (El-Hady et al, 2001). Therefore, these exchangeable cations give rise to adsorption or ion exchange property to the zeolite. The Si/Al ratio of zeolite can vary from 1 to ∞ (Auerbach et al, 2003).

Natural zeolite possesses well defined micropores (XiaoYan et al, 2012), high cation exchange capacity (CEC), adsorption and molecular capabilities (Widiastuti et al, 2011), selectivity, and compatibility with natural environment (Ji et al, 2007; Wang et al, 2007). Theoretical CEC of different zeolites and its ammonium exchange capacity are listed in Table 4.

Table 4: Chemical formula and theoretical CEC of most widely used natural zeolites (Langwaldt, J. 2008).

Zeolites	Chemical formula	CEC (meq/g)	Theoretical NH_4^+ exchange capacity (mg/g)
Chabazite	$(\text{Na}_6\text{K}_6)(\text{Al}_{12}\text{Si}_{24}\text{O}_{72}) \cdot 40\text{H}_2\text{O}$	3.86	72.1
Clinoptilolite	$(\text{Na}_3\text{K}_3)(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	2.22	41.5
Eronite	$(\text{Na}_3\text{Ca}_3\text{K}_2)(\text{Al}_9\text{Si}_{27}\text{O}_{72}) \cdot 27\text{H}_2\text{O}$	3.16	59
Mordenite	$(\text{Na}_8)(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	2.91	54.4

The adsorption mechanism in zeolite is complex in nature. Different physiochemical mechanism such as electrostatic and van Der Waals forces, H-bonding, cation bridges and water bridges are responsible for it. [Koubaisyy et al, 2012].

IE property of zeolite was first investigated by Eichorn in 1858 (Sarioglu, 2005), but only came to scientist and engineers' attention in the mid-20th century (Cincotti, 2001). Zeolite was first used in the early 1970s for removing NH_4^+ in wastewater (Wen et al, 2006). IE capacity of zeolites depends on several factors such as origin, framework structure, ion shape and size, charge density of the anionic framework, ionic charge, and concentration of external solution.

Around the world, more than 40 different types of natural zeolites have been identified (Chojnacki, 2004; Auerbach et al, 2003). Some of them are shown in Figure 11. The properties of different zeolites vary according to their origin, structure, degree of hydration, a variety of dimension, and presence of clay and other slime particles (Chojnacki, 2004). Due to chemical and mineralogical variation of zeolites, only clinoptilolite, modernite and chabazite are considered for commercial products (Christidis et al, 1999).

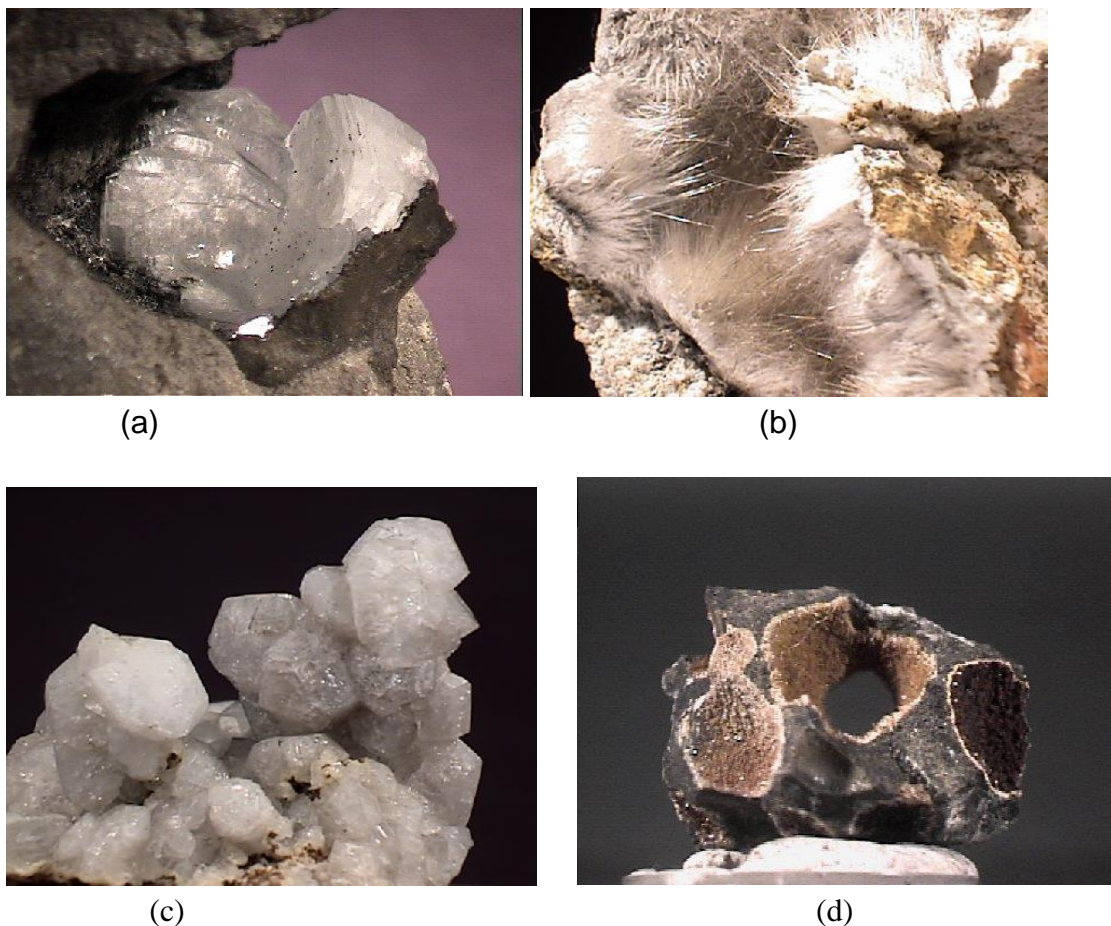


Figure 11: Natural zeolite structures: (a) Clinoptilolite; (b) mordenite; (c) Chabazite; (d) Erionite (Marget et al, 2013)

Natural and synthesized zeolites have been widely used for IE and separation technology. In the past 20 years, natural zeolites have been extensively studied for the purpose of wastewater treatment (Ji et al, 2007). The interest in natural zeolites materials is increasing with the increasing demand for low cost IE and adsorbent materials. Natural zeolites have been applied in various applications such as adsorption, catalysis, building industry, agriculture, soil remediation and energy. The major environmental applications and related studies of natural zeolite particularly in wastewater treatment are summarized in Table 5. The world natural zeolites consumption was predicted to reach 5.5 Mt by 2010 (Wang & Peng, 2011).

Table 5: Environmental application of natural zeolites

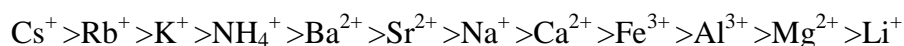
Wastewater treatment	References
Ammonia removal	Chang et al, 2009; Cincotti, et al, 2001; Cooney & Booker, 1999; Cyrus & Reddy, 2011; Demir et al, 2002; Du et al, 2005; Liu & Lo, 2006
Recovery and removal of heavy metal	Cincotti, et al, 2001; Curkovic et al, 1997; De Villiers et al, 1997; Chojnacki et al, 2004; Medvidovic et al, 2006; Merrikhpour & Jalali, 2013
Microorganism removal	Venglovsky et al, 1999; Vargova et al, 1999; Widiastuti et al, 2008
Radioactive element removal	Pansini, 1996; Chalupnik et al, 2013; Dyer & Mikhail, 1985

5.1 Clinoptilolite

Clinoptilolite is one of the most important zeolite and occurs in abundant and highly pure form around the world (Cyrus & Reddy, 2011; Gunay, 2007; Ji et al, 2007). It belongs to heulandites group of minerals and usually found in diagenetically altered pyroclastic rocks (Bedelean et al, 2010). It has Al_2SiO_5 cage like structure and shows significant microporosity (Ji et al, 2007). The unit cell composition of clinoptilolite is $(\text{Na}, \text{K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$ (Dyer & White, 1999). It is very stable towards dehydration and thermally stable to the temperature of 700°C in the air (Ji et al, 2007). The Si/Al ratio of clinoptilolite is 5.7 (Zabochnicka & Malinska, 2010).

It is most frequently used natural zeolite especially for removal of cations such as heavy metals and NH_4^+ ions in aqueous solutions (Demir et al, 2002). The cations present on clinoptilolite are usually Ca, Na and K (Sarioglu, M, 2005). The NH_4^+ ions can selectively exchange Na^+ , Ca^{2+} and Mg^{2+} ions from clinoptilolite than other ions. The high selectivity of clinoptilolite against NH_4^+ can be explained using three mechanisms: molecular size properties, hydration of cations, and anionic corner separation (Si/Al ratio) (Celik et al, 2001).

Clinoptilolites are made up of 8 rings and 10 electrons or 5.6\AA unit window which makes it ideal for NH_4^+ ion exchange (Celik et al, 2001). It has theoretical CEC of about 2.16 mequiv/g (Jha & Hayashi, 2009) and around $4-5 \times 10^{-12} \text{ m}^2/\text{s}$ effective diffusion coefficient for NH_4^+ and Na^+ ions (Balci & Dincel, 2002). The selectivity order of clinoptilolite for cations is in the following order (Cyrus & Reddy, 2011; Sarioglu, 2005; Hedström, 2001; Wang et al, 2006):



The CEC of clinoptilolite depends on many factors such as nature of cations (size, load), temperature, concentration of cations in solution, and structural characteristics of zeolite (Sarioglu, 2005). Usually, natural clinoptilolite has lower CEC compared with some other zeolites but has high selectivity for NH_4^+ ions (Jha & Hayashi, 2009; Wang

et al, 2007; Ji et al, 2007). Also, presence of impurities like quartz in natural clinoptilolite deposited reduces uptake of NH_3 . NH_3 uptake capacity of Na form of clinoptilolite can be increased by adding citric acid and whey proteins (Jha & Hayashi, 2009). The usual method of upgrading clinoptilolite to high cation exchanger is fusion with sodium hydroxide (NaOH) prior to hydrothermal reaction (Wang et al, 2007). Industrially, clinoptilolite was first used in IE unit at Lake Tahoe in Nevada, the US which had 22,700 t/d capacities (Celik et al, 2001).

The most suitable form of clinoptilolite for NH_3 removal is Na form (Sarioglu, 2005; Ji et al, 2007). Hence, most researches are focused on Na form of clinoptilolite for removable of NH_3 .

5.2 Synthetic zeolite

Industrial applications of zeolites require certain specifications. To fulfill these “requirements” zeolites can be synthesized from natural silica and volcanic glasses (Christidis et al, 1999) or natural zeolites are modified using various technologies such as acid and alkali treatments, salt, thermal, surfactant and microwave modification (Huo et al, 2012). The advantages of synthesized zeolites over natural ones are constant composition of products (Christidis et al, 1999).

Synthesized zeolites have uniform micropore structure and high surface area (Figure 12). It has high Q compared with natural zeolite and many researches has been carried out for synthesis of zeolites from coal ash, asbestos, fly ash, metakaolinite, rice husk, etc. However, synthesized zeolite is not contamination free. Contaminations such as residual raw materials have potential to reduce CEC and applicability of synthetic zeolites. [Zhao et al, 2010].

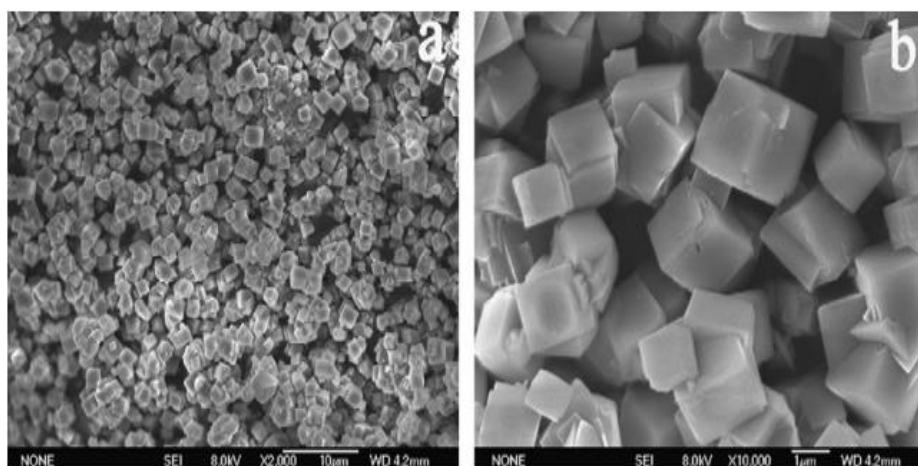
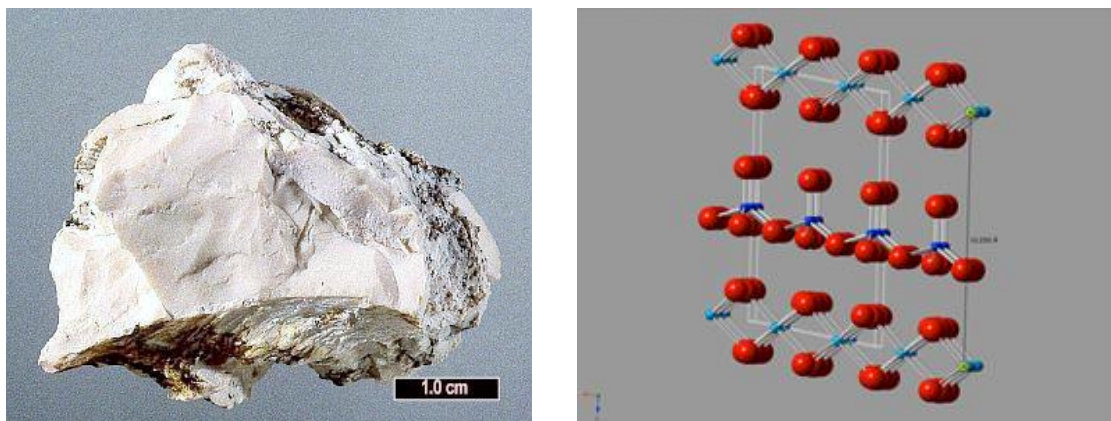


Figure 12: Synthesized NaA zeolite (Zhao et al, 2010)

5.3 Halloysite

Halloysite ($\text{Al}_2\text{SiO}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) is a part of kaolinite clay mineral group (Kamble et al, 2012). It is composed of 1:1 dioctahedral Al_2SiO_5 layer (Zhao et al, 2010). They occur in different shape and hydration state (Joussein et al, 2005). For example: 10\AA and 7\AA are hydrated and dehydrated forms of halloysite as shown in Figure 13 (Hillier & Ryan, 2002). The natural deposits of halloysite are China, New Zealand, America, Brazil, and France (Rawtani & Agrawal, 2012). CEC of halloysite is affected by place of origin and hydration state.



(a)

(b)

Figure 13: Images of halloysite (a) Halloysite; (b) mixed layer of hydrated and dehydrated form of halloysite (<http://clay.uga.edu/courses/8550/CM07.html>)

Halloysite is an important member of kaolinite group because of its nanotechnology applications. Halloysite is used in personal care and cosmetic products, anticancer therapy, sustained delivery for certain agents, acts as template or nano reactors for biocatalyst, and environmental protection (Kamble et al, 2012).

5.4 Bentonite

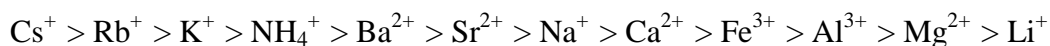
Bentonite has a high CEC and belongs to the 2:1 smectite clay mineral groups. It is mainly composed of montmorillonite. The basic structural unit of bentonite is made of the Al_2SiO_5 framework where the Al octahedral layer is present between tetrahedral layers of Si (Figure 14). The isomorphous substitution of Si_4^+ by Al_3^+ in the tetrahedral layer and Al^{3+} by Mg^{2+} in the octahedral layer generates negative charge on the clay. Cations are required to compensate negative charges of the laminar edge which gives higher adsorption ability to bentonite. [Bourliva et al, 2010; Qian et al, 2006]. The chemical and mineralogical composition is shown in Table 6.

6. COMPETITION WITH OTHER CATIONS

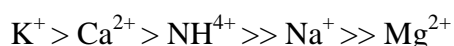
Wastewater is a complex mixture of different types of substances such as salts (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}), metals (e.g., Cu, Pb, Zn, and Fe) and anions (RCOO^- , Cl^- , SO_4^{2-} , and PO_4^{3-}). These substances act as competitive ions and their presence effect NH_3 removal by zeolite which can be better explained with selectivity series. If we look at selectivity series of clinoptilolite and chabazite, these zeolites show higher selectivity towards K^+ than NH_4^+ . Hence, presence of K^+ cations will decrease the NH_4^+ removal capacity of the system. Similarly, in presence of metals, lead (Pb) show higher selectivity to zeolite compared with NH_4^+ . But, in general wastewater contains very low concentration of Cr, Ni, Pb and Cd and higher concentration of Zn and Cu (Wang et al, 2005). Therefore, from selectivity order of metal by zeolite, it can be said that metals effect on NH_4^+ uptake by zeolite is negligible.

The selectivity series for anions and modified zeolites are also presented below. The adsorption of other ions reduces uptake capacity of NH_3 and affects the economy of the process as a whole.

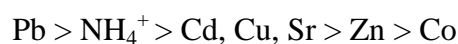
The selectivity order of clinoptilolite (Bedeleian et al, 2010; Cyrus & Reddy, 2011; Sarioglu, M. 2005; Hedström, 2001; Wang et al, 2006):



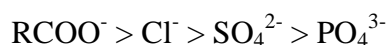
The selectivity order of chabazite (Levy-Ramos et al, 2010):



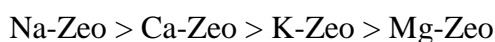
The selectivity order of metal (Cincotti et al, 2001)



The selectivity order for anions (Huang et al, 2010)



The NH_3 exchange capacity of modified zeolite is in the order (Leyva-Ramos et al, 2001):



The cation selectivity of zeolite depends upon various factors such as atomic charge (Nasfer & Ujang, 2012), atomic number (Langella et al, 2000), ionic radius and electronegativity ((Merrikhpour & Jalali, 2013).

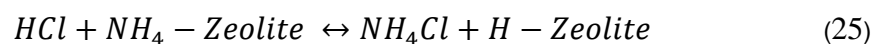
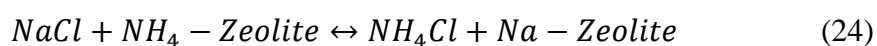
- (i) Atomic charge: selectivity increases with the increase in charge on exchanging cation, which means divalent ions are held more strongly than univalent ions.
- (ii) Atomic number: selectivity increases with the increase in the atomic number.
- (iii) Ionic radius: decrease in the radius of hydrated ions in solution increases adsorption by exchanger
- (iv) Electronegativity: higher electronegativity of the cations allows for more interaction with adsorbent.

7. REGENERATION

Regeneration of NH_4 -zeolite is an important step in wastewater treatment for sustainability of the system. $\text{NH}_4^+/\text{NH}_{3(\text{g})}$ E% of zeolites decreases when it is used for a long period, mainly because zeolite gets saturated or exhausted with NH_3 . Hence, it should be regenerated before reusing it. Regeneration involves removing and replacing exchanged ions (in our case NH_4^+) with ions that place zeolite in the desired form for reuse again. Regeneration can be carried out either in an upflow or downflow mode. Long term efficiency and good regeneration ability of zeolite is important to reduce cost in wastewater treatment (Bolan et al, 2003). There are different methods for regenerating absorbent materials such as chemical, biological, and heating regeneration.

7.1 Chemical Regeneration

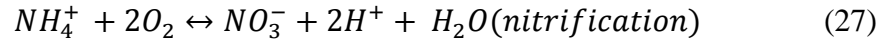
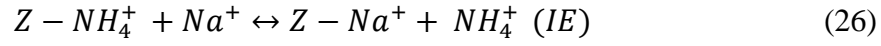
Chemical regeneration is carried out using acid (e.g., HCl , H_2SO_4) or alkali (e.g., NaOH , NaCl , Ca_2Cl) chemicals. Zeolite regeneration using chemicals have been investigated in several studies (Cyrus & Reddy, 2011; Rahmani et al, 2009; Bolan et al, 2007; Li et al, 2011; Siljeg et al, 2010; Ji et al, 2007). The most commonly used regeneration chemicals are NaCl and HCl . In NaCl regeneration process, Na^+ ion is exchanged with NH_4^+ ion adsorbed in zeolite (equation 24). Hence, NH_4^+ removing property of zeolites is restored. Similarly in HCl regeneration, H^+ ions are exchanged with NH_4^+ ions in zeolite as shown in equation 25.



Chemical regeneration is an expensive process as treatment and disposal of concentrated NH_4 -brine solution demands a high cost (Rahmani et al, 2009). Similarly, increased concentration of Cl in effluent can demand high cost in wastewater treatment plants as Cl has adverse effects on organisms living in water and in soil even at low concentrations (U.S.EPA, 1994).

7.2 Biological Regeneration

Biological regeneration is carried out in presence of nitrifying bacteria. It operates in two steps: IE and nitrification (equation 26 and 27). Biological regeneration can be carried out in a single reactor or multireactor systems (Lahav & Green, 1998; Lahav & Green, 2000; Hedström, 2001).



Zeolite acts as carrier for nitrifying bacteria in the regeneration process. These microorganisms can only oxidize NH_4^+ into NO_3^- , which is released in the solution in oxygen rich environment (Widiastuti et al, 2008), but cannot keep up with high load. Hence, zeolites will adsorb the NH_4^+ overdose. When NH_4^+ concentration in the solution drops, NH_4^+ dissolves in the regenerant solution and will be converted into NO_3^- by the bacteria. Therefore, cation containing regenerant is recirculated through the bed in order to desorb NH_4^+ into the solution. The recirculation process continues until NH_4^+ concentration in the solution drops to negligible value. The schematic representation of a biological regeneration is shown in Figure 15 (Lahav & Green, 1998; Lahav & Green, 2000; Hedström, 2001). The nitrate-rich backwash solution is stored for reuse or can be easily disposed of (Rahmani & Mahvi, 2006; Lahav & Green, 1998; Lahav & Green, 2000; Hedström, 2001).

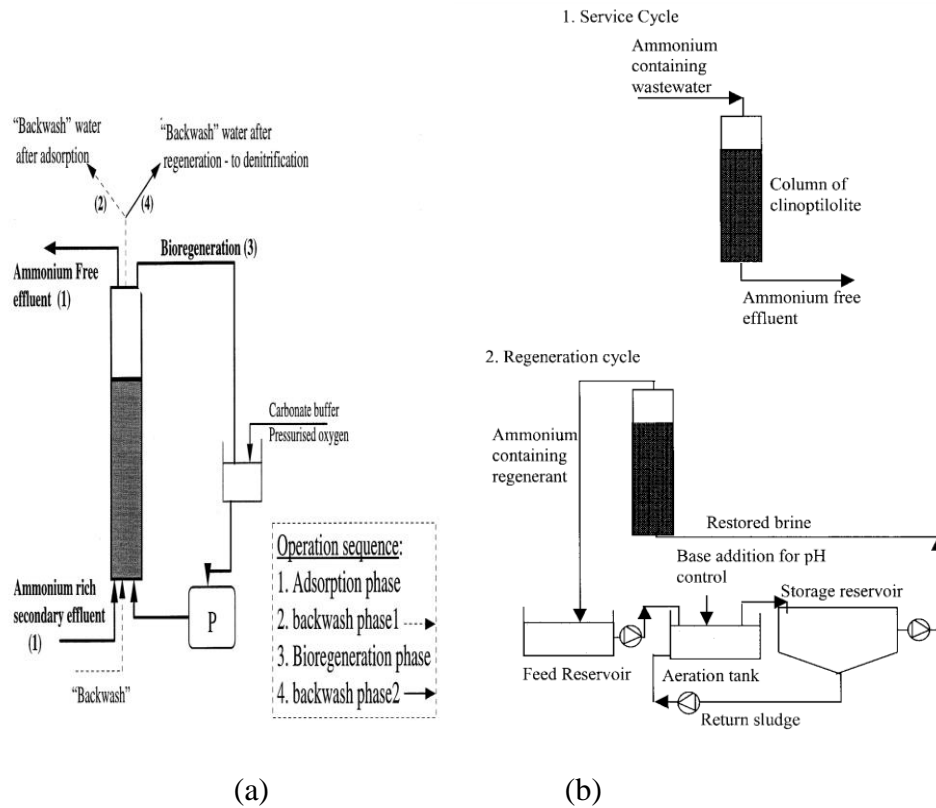


Figure 15: Bioregeneration types (a) single reactor (Lahav & Green, 1998; Lahav & Green, 2000) & (b) multi-reactor (Hedström, 2001).

8. MODELS

Models are necessary to extract information on design and operation of the process. It gives insight to performance capacity of the systems.

8.1 Isotherm models

The isotherm study is required to characterize the equilibrium relationships between the amount of exchanged ion by zeolite and its equilibrium concentration in solution (Malekain et al, 2011; Huang et al, 2010; Kucic et al, 2012). The exchange of NH_3 can be studied by using different types of equilibrium isotherm models such as Freundlich, Langmuir, Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Sips, Khan, Hill, Flory-Huggind and Radke-Prausnitz isotherm (Foo & Hameed, 2010). Freundlich and Langmuir isotherm models are the most commonly used method for analyzing equilibrium data (Du et al, 2005; Zheng et al, 2008; Sarioglu M, 2005; Karadag et al, 2006; Zhao et al, 2010).

8.1.1 Freundlich adsorption isotherm

Freundlich isotherm is applied to multilayer adsorption with non-uniform distribution over the heterogeneous surface. It gives a logarithmic relationship between the solid and solution concentrations. It is helpful in correlating isotherm data collected over a wide range of concentration. Freundlich equation can be written as in equation 28 [Du et al, 2005]:

$$q_e = K_f C^{1/n} \quad (28)$$

Where, q_e is the amount of NH_4^+ adsorbed per unit weight of zeolite (mg/g); C is the equilibrium concentration of NH_4^+ remaining in solution (mg/l); K_f is Freundlich constant (mg/g) and $1/n$ is the heterogeneity factor and represents adsorption capacity of adsorbent and a constant relating to adsorption intensity or surface heterogeneity respectively.

Freundlich equation can be rearranged to linear form by taking logarithms on both sides as in equation 29 [Du et al, 2005; Zheng et al, 2008]:

$$\log Q = \log K_f + \frac{1}{n} \log C \quad (29)$$

8.1.2 Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption with the uniform distribution of energetic adsorption sites. It can be written as (equation 30) (Sarioglu, 2005):

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (30)$$

Where, q_e is the equilibrium amount of NH_4^+ exchanged by zeolite (mg/g), C_e is the equilibrium concentration of NH_4^+ in the solution (mg/L), q_{max} is the maximum uptake of ammonia exchanged and K_L is the Langmuir constant (L/mg) which is calculated from slope and the intercept of the linear plot.

Langmuir equation can be rearranged into the liner form (equation 31) (Karadag et al, 2006; Zhao et al, 2010; Zheng et al, 2008):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (31)$$

The dimensionless constant known as a separation factor (R_L) is used to express the essential features of Langmuir isotherm which is given in equation 32 (Zheng et al, 2008; Zhao et al, 2010; Foo & Hameed, 2010).

$$R_L = \frac{1}{1 + K_L C_0} \quad (32)$$

Where C_0 (mg/L) is initial concentration of NH_4^+ and K_L is the Langmuir constant (L/mg). There are four possible outcomes of R_L value that is (i) $0 < R_L < 1$; favorable adsorption, (ii) $R_L > 1$; unfavorable adsorption, (iii) $R_L = 1$, linear adsorption and (iv) $R_L = 0$, irreversible adsorption.

8.2 Kinetic models

Kinetic models provide the base to determine the performance of both fixed and continuous systems. Kinetic analysis of the adsorbent gives an idea about a reaction pathway, solute uptake rate, significance for the pilot application, and scale of an adsorption apparatus. Numerous sorption models have been developed and investigated. [QIU et al, 2009; Ho & McKay, 1999].

8.2.1 Pseudo first order kinetic model

In 1898, Lagergren presented first order rate equation based on adsorption capacity to describe the kinetic process of solid and liquid phase adsorption. It can be represented as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (33)$$

Integrating boundary conditions of $t=0$ to $t=t$ and $q_i=0$ to $q_t=q_t$ in equation 33. It can be rearranged for linearized data plotting as shown in equation 34.

$$\log[q_e - q_t] = \log[q_e] - \left[\frac{k_1}{2.303} \right] t \quad (34)$$

Where, k_1 is a rate constant of pseudo-first-order model (min^{-1}), q_t and q_e are the amounts of NH_4^+ ions adsorbed onto zeolite at time t and at equilibrium (mg/g), respectively. k_1 and calculated q_e values are determined from the slope and intercept of the $\log(q_e - q_t)$ versus t plot. [QIU et al, 2009; Ho & McKay, 1999; Edrozan & Ulku, 2011].

8.2.2 Pseudo second order kinetic model

In 1995, Ho explained a kinetic process of adsorption using the pseudo second order kinetic model (QIU et al, 2009). It is assumed that the sorption capacity is proportional to the number of active sites occupied on the sorbent. It can be expressed as follows (Ho & McKay, 1999):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (35)$$

After integration and applying boundary conditions of $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ in equation 35. It can be rearranged for linearized data plotting as shown in equation 36.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (36)$$

Where, k_2 is rate constant of pseudo-second-order models ($\text{g}/(\text{min}.\text{mg})$), q_t and q_e are the amounts of NH_4^+ ion adsorbed onto zeolite at time t and at equilibrium (mg/g), respectively. k_2 and calculated q_e values are determined from the slope and intercept of t/q_t versus t plot.[Edrozan & Ulku, 2011].

9. MATERIAL AND METHODS

9.1 Wastewater

Wastewater was collected from Viinikanlahti Wastewater Treatment Plant, Tampere, Finland. The plant started its treatment process in 1972 with mechanical treatment and later upgraded into chemical treatment in 1976. Biological-chemical treatment was introduced in 1982 and biological and pretreatment parts were renovated and expanded in 2003. [Katko & Juuti, 2007]. The wastewater treatment plant has the pre-clarification capacity of 120,000 m³/day and biological treatment of 67000 m³/day (Golemanov & Zgodavova, 2003).

We sampled several times the return sludge from the secondary settling to incorporate any possible seasonal variations. The wastewater was allowed to settle at room temperature for an hour. The supernatant from the settled sludge was collected in clean containers using peristaltic pumps (G.W.Berg& Co., Finland). The collected supernatant was filtered through 47 mm glass filter (GF/A) (Whatman, UK). Filtered and unfiltered samples, and settle sludge were stored at -4°C until further use.

Samples were spiked with ammonium chloride (NH₄Cl) to reach the desired concentration. Unless otherwise mentioned, all the batch and column experiments were carried out using filtered wastewater.

9.2 Analytic methods

9.2.1 Reagents

All the reagents used in the experiments were analytical grade reagents. All the solutions required for experiments were prepared using Milli-Q (MQ) water and stored under proper condition until further use.

9.2.2 Total Solids

Total solids (TS) were determined from wastewater as described in Standard Methods 2540 (APHA 1999). The empty dishes were dried in 105°C oven for two hours and stored in desiccators until further use. Before use, the dried dishes were weighed with a balance (Scaltec SBC 31, Germany). To the weighed dishes, 5 ml of well mixed sample was added and dried in 105°C oven for overnight (Figure 16). The dishes were removed from the oven and cooled in desiccators for an hour. Then, the dishes were weighed

with a balance. TS were always measured in duplicates. TS were calculated using equation 37.

$$TS \left(\frac{mg}{l} \right) = \frac{(A-B) \times 1000 \times 1000}{V} \quad (37)$$

Where, A is weight of dried residue and dish (105°C) (g), B is weight of dish (g) & V is volume of sample (ml)

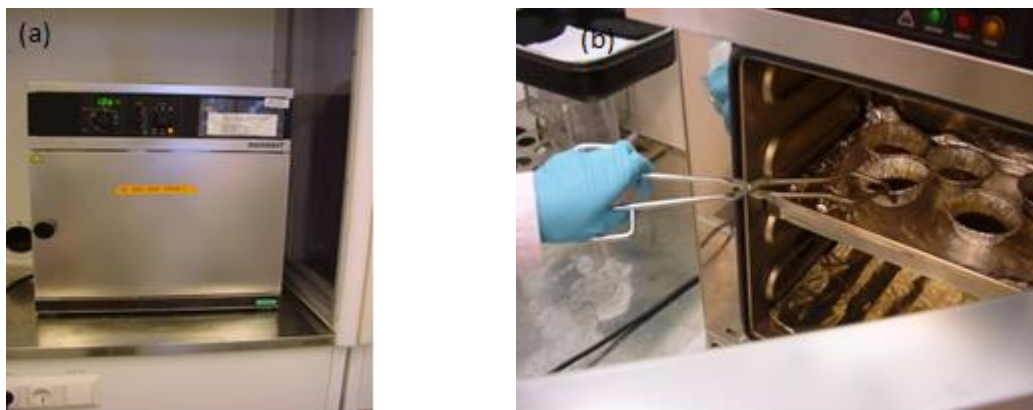


Figure 16: Solids measurement (a) oven (0-300°C); (b) sample + dish

9.2.3 Ammonia/ammonium

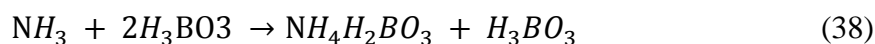
NH₃/NH₄⁺ measurements were used to determine the amount of NH₃/NH₄⁺ in the influent, effluent sample of IE, and of regeneration. NH₄⁺ and NH₃ in the sample were determined by using distillation-titration and NH₃ electrode methods respectively. Distillation-titration method was used for batch study and NH₃ electrode method was used in column study. Standard tests were carried out to check if there was variation between the results obtained with both methods (Table 7). Since, the differences between the results of both methods were minimal; any method can be used for NH₃/NH₄⁺ detection in the experiments.

Table 7: Results of standard sample testing using electrode and distillation method

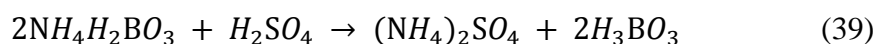
Sample	NH ₄ -N (mgN/L)			Standard deviation (mgN/L)	% error
	Calculated	distillation	Electrode		
1	53	48	53	2.7	5.3
2	148	143	143	0.2	0.2
3	302	279	279	0	0
4	519	517	509	4.1	0.8
5	1048	1042	1044	0.7	0.1
6	1534	1523	1556	16.3	1.1

9.2.4 Distillation-titration method

Distillation and titration method was carried out using KjeltelTM 2100 (Foss, Denmark). In the distillation unit (Figure 17), NH_3 is converted into NH_4^+ in presence of alkali (NaOH, 32%). The distillation time and alkali addition were preprogrammed in the distillation unit. Boric acid solution (H_3BO_3) was used to capture NH_3 forming ammonium borate ($\text{NH}_4\text{H}_2\text{BO}_3$) complex in presence of NaOH (equation 38). NH_4^+ entrapping changes H_3BO_3 from pink to a green color.



The titration of $\text{NH}_4\text{H}_2\text{BO}_3$ complex with standard sulfuric acid (H_2SO_4) neutralizes the complex and changes solution into its original color (equation 39). [LABCONCO, 2013].



The amount of H_2SO_4 consumed in this process is directly proportion to the NH_4^+ ion concentration. The $\text{NH}_4\text{-N}$ was calculated according to equation 40.

$$\text{NH}_4 - \text{N} \frac{\text{mgN}}{\text{L}} = \frac{T \times N \times 14.007 \times 1000}{V_{\text{sample}}} \quad (40)$$

Where, T is titration volume of H_2SO_4 (ml), N is normality of H_2SO_4 , 14.007 is the molar mass of N, and V_{sample} is volume of the sample to be tested.

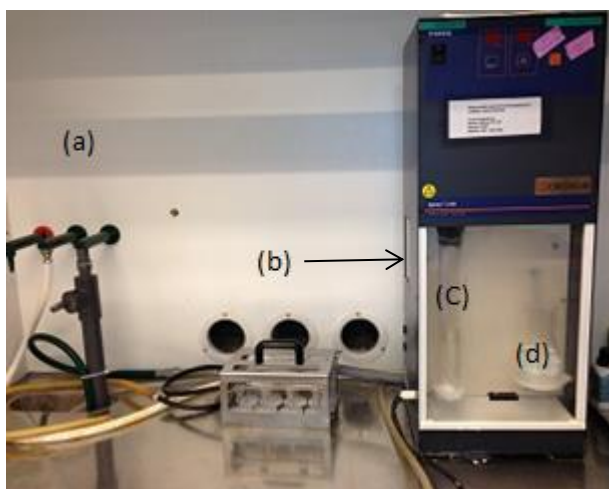
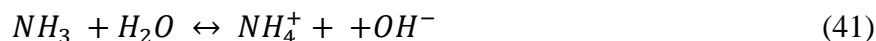


Figure 17: Distillation Method (KjeltelTM 2100 (Foss, Denmark) (a) water (b) distillation unit (c) glass tube with sample & (d) Erlenmeyer flask with boric acid.

For distillation of each time interval, 25 ml sample was added in a Foss glass tube, followed by addition of 40 ml of NaOH to increase the pH of the solution above 11. NH_4^+ was entrapped in 25ml H_3BO_3 in Erlenmeyer flask. The sample after distillation was titrated against standard H_2SO_4 and the pH of final solution was 4.6.

9.2.5 Ammonia electrode

NH₃ dissolved in solution diffuses through the hydrophobic gas permeable membrane in the electrode and dissolves in the filling solution until the partial pressure is the same on both sides of the membrane. NH₃ diffusing through a membrane also reacts with water in the filling solution as shown in equation 41. [Orion 95-12].



The experimental setup for NH₃ test using NH₃ electrode is shown in Figure 18. To measure samples with NH₃ electrode, 500 ml of 0.1M and 0.5M NH₄Cl standards were prepared and stored at -4°C until further use. The lower (1:100) and upper (1:10) limits in electrode was calibrated with the standard solution (0.1M or 0.5M NH₄Cl). Prior to NH₃ measurement, 2 ml ionic strength adjuster (ISA) was added to sample and NH₃ electrode was kept at 45° angles to prevent air bubbles formation on the membrane. An addition of ISA increases pH of the solution above 11 and converts NH₄⁺ to NH_{3(g)}. After adding ISA, the beaker was covered with a parafilm to minimize loss of NH_{3(g)} in the air and stirrer gently and the readings were taken exactly after 3 minutes of measuring. After calibrating lower and upper limits, experimental samples were measured in the same manner. For detail information on measurement, see Orion 95-12 manual. The electrode was kept in 0.1 M NH₄Cl solution for overnight storage and the electrode membrane and inner membrane filling solution were replaced every 3rd week or as needed.

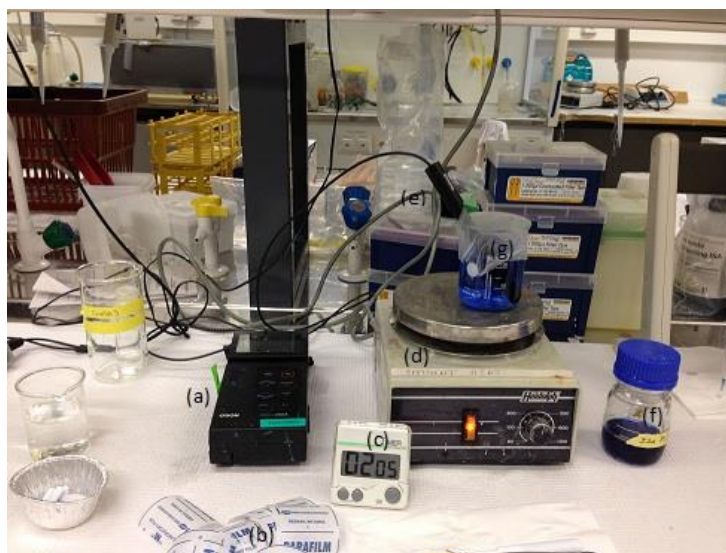


Figure 18: Experimental set up for ammonia test using NH₃ electrode (Orion95-12, Thermo) (a) meter; (b) parafilm; (c) timer; (d) magnetic stir; (e) NH₃ electrode; (f) ISA; (g) beaker with sample, NH₃ electrode, and magnetic rod

The mV reading of NH₃-N was converted into mg/l by using Prediction Method, that is, FORECAST function in excel 2010. Multiplication of dilution factor and antilog of FORCAST value gives mg/l concentration of NH₃-N in the effluent sample.

9.2.6 Nessler Method

The Nessler method has been widely used to test NH_4^+ concentration in water. In Nesslerization process, K^+ , mercury (Hg), and iodine (I) react with NH_4^+ to give yellow-brownish colored compound. The intensity of color is proportional to NH_4^+ concentration of the sample. [Jeong et al., 2013]

The sample is buffered to alkaline pH 9.5 to decrease the hydrolysis of cyanates and organic N compounds. The sample was distilled into a solution of H_3BO_3 . NH_3 distillate was then nesslerized by adding nessler reagent. Then, the concentration of NH_3 is measured using standard spectrometric measurement (Figure 19) or colorimetrically by Nesslerisation.



Figure 19: Spectrophotometric determination of NH_3

9.3 pH

The pH is an important parameter in cation exchange of wastewater as it is responsible for the predominance of an element at a given pH. Cation exchange process can remove only ionized forms of NH_3 (Sprynskyy et al, 2005). The pH of the wastewater was measured with a WTW, 330i pH meter with pH-electrode Sen Tix 41. pH of the sample was measured at the beginning of each experiment. The electrode was stored in 3mol/l KCl solution when not in use.

9.4 Ion Exchange material

In our lab in Tampere University of Technology (TUT), we tested NH_3 removal method using different types of natural adsorbent (e.g., Zeolite, halloysite and bentonite). Zeolite had far better E% and Q compared to halloysite and bentonite. Therefore, in this work, different particle sizes of natural zeolites were used to study $\text{NH}_4^+/\text{NH}_3$ removal from municipal wastewater. Batch and column methods were used to study the adsorption capacity or removal efficiency of zeolite particles.

9.4.1 Zeolite

Natural zeolites used in the experiments were from zeolite supplier Zeocem®, Slovak Republic. The chemical and mineral composition of zeolite is presented in Table 8. Zeolites of two different particle sizes: 0.2-0.5 mm (Figure 20 (a)), and 0.6-2.0 mm (Figure 20 (b)) were used for both batch and column experiments. Zeolite particles were washed and dried in an oven before the experiments.

Table 8: Chemical & mineral composition of natural zeolite (Zeocem®)

Chemical composition		Mineral composition	
SiO ₂	65.00 – 71.30 %	Clinoptilolite	84 %
Al ₂ O ₃	11.50 – 13.10 %	Cristobalite	8 %
CaO	2.70 – 5.20 %	Clayish mica	4 %
K ₂ O	2.20 – 3.40 %	Plagioclase	3-4%
Fe ₂ O ₃	0.70 – 1.90 %	Edisonite	0.10-0.30%
MgO	0.60 – 1.20 %		
Na ₂ O	0.20 – 1.30 %		
TiO ₂	0.10 – 0.30 %		
Si/Al	4.4 – 5.4		

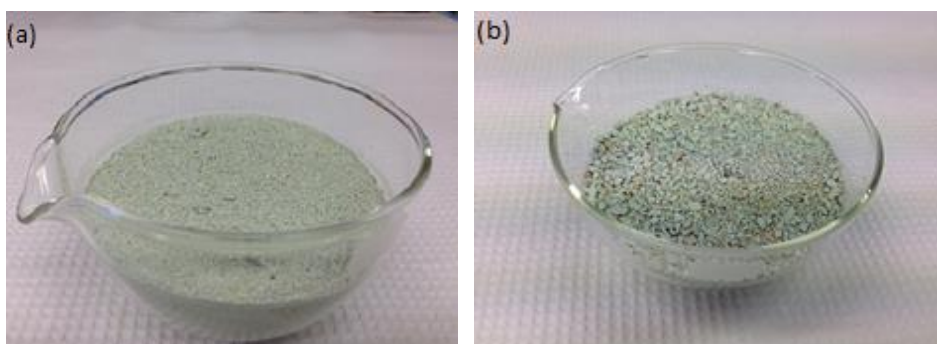


Figure 20: Zeolite particle sizes: (a) 0.2-0.5mm and (b) 0.6-2.0mm

9.4.2 Batch experiment

The batch experiments were conducted to study the effects of NH₄⁺ load, pH, particle sizes (0.2-0.5 mm and 0.6-2.0 mm), and solids on zeolite performance. The batch experiments are shown in Figure 21. All the experiments were carried out in duplicate at room temperature. Both zeolite types were washed 5 times with tap water to remove any non-adhesive impurities and small particles and then dried at 105°C for 12 hours to remove the moisture.

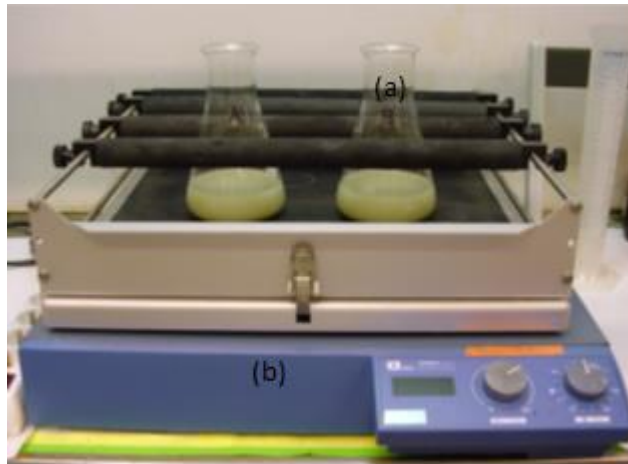


Figure 21: batch experiment: (a) conical flask with sample and zeolite; and (b) shaker.

The batch experiments were performed by mixing 500 ml sample with 50 g zeolite in 1000 ml Erlenmeyer flask at 156 ± 2 rpm in shaker (KS501 digital IKALABORTECHNIK) for 2 hours. 50 ml supernatant was withdrawn from the batch assays at pre-defined time interval (5, 10, 20, 30, 45, 60 and 120 minutes) to determine the amount of residual NH_4^+ . Prior to withdrawal of a sample, the shaker was stopped for 3 minutes to allow the samples to settle. NH_4^+ concentration in the withdrawn samples was analyzed using the distillation- titration method (ISO 5664:1984).

The NH_4^+ exchange capacity (q_t and q_e) and removal $E\%$ of zeolite were calculated using equations 42-44 (Huang et al, 2010):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (42)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (43)$$

$$E\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (44)$$

Where, q_t and q_e are the total amount of adsorbed NH_4^+ ions per unit weight of zeolite at time t and at equilibrium (mg/g) respectively, C_0 , C_e and C_t are initial, equilibrium, and concentrations of NH_4^+ at time t in the solution (mg/L), respectively, V is the volume of working solution (L), m is adsorbent mass (g), and E is NH_4^+ removal efficiency expressed in %.

9.4.2.1 Effect of ammonium load

Experiments were carried out on filtered samples to determine the effect of NH_4^+ load on the IE process. Varying NH_4^+ concentrations were achieved (250, 500, 750, 1000, 1500, 2000 and 2500 mg/L) by dissolving pure NH_4Cl in the desired volume of wastewater. 500 ml of individual sample concentrations was poured in 1000 ml Erlenmeyer flask with 50 g zeolite and stirred at 156 ± 2 rpm for two hours. The initial pH of the sample was in the range of 7.0 ± 0.5 . The experiments were conducted as mentioned in Section 9.4.2.

9.4.2.2 Effect of pH

To determine the pH effect on the IE process, filtered samples were adjusted with 1M H_2SO_4 or 1M NaOH to pH of 6, 6.5, 7, 7.5 and 8.5. The pH effect on zeolite activities was determined at constant NH_4^+ load (1500 mg/L) and mixing speed of 156 ± 2 rpm. The experiment was conducted as mentioned in Section 9.4.2.

9.4.2.3 Effect of TS

This experiment was conducted to study the effect of solids on zeolite capacity. To study the effect of TS, settled sludge was used as original sample (100%). The 100% original sample had 26900 mg/l TS. Samples with various TS concentrations (5, 7.5, 10, 15, 20, 30, 50, and 75 %) were prepared by mixing original sample and unfiltered supernatant at a different ratio (wt/wt). The effect of TS on zeolite was studied at constant NH_4^+ concentration (750 mg/l), pH (7.2 ± 0.3), and agitation speed of 156 ± 2 rpm. The experiments were conducted as explained in Section 9.4.2.

9.4.3 Column experiments

The column experiments were conducted using two different zeolite classes (particle size 0.2-0.5 mm and 0.6-2.0 mm) to study the effect of flow rate, pH, and regeneration on NH_3 removal capacity of zeolites. The general operational conditions for both zeolites types are shown in Table 9. The concentration of residual NH_3 was determined by using NH_3 Selective Electrode as described in Section 9.2.5. Zeolite particles were washed 10 times with DI water and dried at 105°C for 24 hours. All the experiments were performed at fixed NH_4^+ load (1500 mg/L) and new columns were prepared for each flow rate and pH experiment. The desired volume of the sample was passed through the column to achieve NH_3 breakthrough at 30% of initial concentration.

Table 9: Operational conditions of column experiments

Column material		glass
Column height	cm	55
Internal diameter	cm	5.4
Bed height	cm	14.5
Area of column	cm^2	22.89
Total bed volume	cm^3	331.91
adsorbent		zeolite
Mass of adsorbent	g	300
Particle size	mm	0.2-0.5 or 0.6-2.0
NH_4Cl	mg/l	1500
Type of pump		Peristaltic pump
Mode of flow		downflow

The adsorption capacity of the column was calculated using equation 45 (Li et al., 2011):

$$Q = vS \int_0^t (C_0 - C_t) dt \quad (45)$$

Where, Q is the amount of NH_4^+ in the solid phase (mg/g), v is a filtration rate (m/h), S is cross section area of the column (m^2), C_0 and C_t are NH_4^+ concentration before and after passage through the column (mg/L), respectively and t is experiment operation time (h).

9.4.3.1 Porosity

Porosity (n) is the amount of void space within a volume of zeolite. It can be determined using two methods: density and saturation methods.

8.4.3.1.1. Density method

In density method, porosity (ε) is determined from the bulk density (ρ_b) and particle density (ρ_d) of the material. It can be calculated using equation 46. [Cyrus & Reddy, 2011].

$$\varepsilon = 1 - (\rho_b / \rho_d) \quad (46)$$

Since all the required data to calculate porosity using density method was unavailable, this method was not used.

8.4.3.1.2. Saturation method

Porosity using the saturation method was determined by measuring the required water volume to saturate all the pores of zeolite samples. The total porosity was calculated using equation 47 (Sprysky et al, 2005a).

$$n = V_w / V_0 \quad (47)$$

Where, n is the total porosity, V_w is the water volume required to saturated zeolite (cm^3) and V_0 is the total volume of zeolite in the column (cm^3). V_w is obtained by subtracting amount of water in the column in presence of zeolite and glass wool by amount of water in the column without zeolite.

The porosity was calculated as follows: glass wool was placed at the bottom of the column to prevent leakage of the zeolite from the column. Consequently, water was added until it exactly covered the glass wool. The stopcock was opened slowly and the effluent was collected in a beaker. The collected effluent was measured using a measuring cylinder. The process was repeated 5 times. To the same column, 300 g of zeolite was added and water was introduced in the column until it exactly covers the zeolite. The water is then drained, collected and measured as before. The process was repeated 5 times. The porosity of zeolite particles was calculated using equation 47 and average value of the repeated measurement (Table 10).

Table 10: Porosity of zeolite particles

zeolite particle	n
0.2-0.5 mm	0.098
0.6-2.0 mm	0.193

9.4.3.2 Column preparation

The glass column was fixed with the column stand (Figure 22). Glass wool soaked in MQ water was placed at the bottom of the column to provide a base for the zeolite bed. Consequently, 250 ml of MQ was added and air bubbles were removed by gently stirring in circular motion with a rod. Thereafter, 300 g of the conditioned zeolite was poured into 500 ml clean beaker and mixed with 250 ml MQ water. Then, the prepared zeolite slurry was introduced into the column through a funnel. The column was gently stirred in circular motion with a rod to remove air bubbles. The total water volume in the column was approximately 500 ml. Several columns were prepared in similar manners.

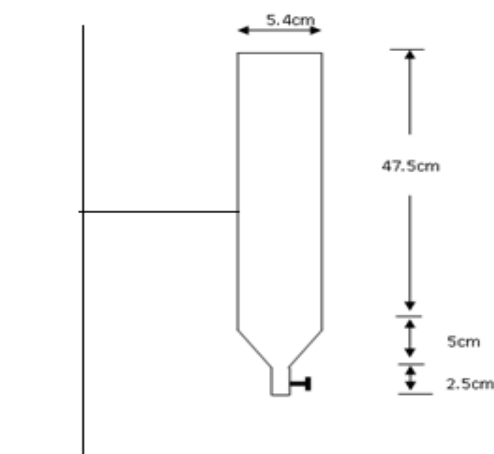


Figure 22: Sketch of the glass column

9.4.3.3 Column run

Samples were passed through the column loaded with 300 g zeolite using a peristaltic pump (Figure 23). The initial 500 ml samples were discarded to remove the MQ water in the column during column preparation. Then effluent from the column was collected at pre-defined volumes (600, 1200, 1450, 1700, 2300, 2800, 3200 and 3700 ml) to measure the concentration of NH_3 . 150 ml sample was collected at 600 ml and 1200 ml predefined volumes and for the rest, 100 ml sample was collected at each predefined volumes. In addition, actual time at which the effluent was collected was recorded simultaneously. NH_3 concentration in collected samples was analyzed using NH_3 electrode as described in Section 9.2.5.



Figure 23: Experimental setup of column study.

9.4.3.4 Effect of flow rate

Samples with fixed NH_4^+ load (1500 mg/L) and pH 6.5 ± 0.1 were studied at different flow rates (10, 20, 30, 40 & 50 ml/minute). The column preparation and experiments for the flow rate were conducted as mention in Section 9.4.3.2 and 9.4.3.3.

9.4.3.5 Effect of pH

Samples with fixed NH_4^+ load (1500 mg/L) and flow rate (25 ± 1 ml/minute) were run at different pH (6, 7, 7.5, 8, 8.5, 9 & 9.5). The pH of the samples were adjusted with 1M H_2SO_4 or 1M calcium hydroxide ($\text{Ca}(\text{OH})_2$). The column preparation and experiments for the flow rate were conducted as mention in Section 9.4.3.2 and 9.4.3.3.

9.5 Regeneration

NH_4^+ removal efficiency of zeolites decreases when it was used for long period. It was mainly because columns get saturated or exhausted with NH_4^+ . The exhausted columns were rejuvenated with NaCl and HCl. To carry out the experiments, desired volume of filtered wastewater was spiked with NH_4Cl to reach a fixed concentration of 1500 mg/l. The pH of the spiked sample was tested before each experiment and was adjusted to pH 7.0 ± 0.1 with 1M H_2SO_4 or $\text{Ca}(\text{OH})_2$.

9.5.1 NaCl regeneration

For the regeneration study, fresh columns were prepared as mentioned in Section 9.4.3.2. Desired volume of sample was passed through the new column at constant flow rate (15 ml/min) as mentioned in Section 9.4.3.3.

The exhausted zeolite was regenerated by back washing the column with 0.5N or 0.1 N NaCl. Prior to the regeneration process, the column was washed with 500 ml MQ

to remove excess NH_4Cl in the eluent remaining in the column. Desired volume of 0.5 N NaCl was passed through the exhausted column at flow rate of 30 ml/min. First, 500 ml effluent was discarded to remove remaining water in the column. Then, effluent from the column was collected at the regular volume interval to measure the concentration of NH_3 at 350, 700, 1050, 1400, 2100, 2600, 3100 and 3600 ml. For all the volume intervals, first 200 ml samples were discarded and last 150 ml was collected. Actual time at which each effluent was collected was also recorded simultaneously. The NH_3 concentrations in collected samples were analyzed using NH_3 electrode as described in Section 9.2.5.

After NaCl wash, 500 ml MQ was passed through the column. NH_4Cl and NaCl wash as mentioned was repeated until 6th regeneration cycle and the system was stopped. All the collected samples in a regeneration process were filtered through 0.45 μm white man filter and stored in -4°C until further analysis.

Similarly, 0.1 N NaCl regeneration was carried out in the same manner as mentioned in Sections 9.5.1. But, the process was stopped after 1st regeneration as the NH_3 adsorption capacity decreased in comparison with initial NH_4Cl run and regeneration with 0.5N NaCl.

9.5.2 HCl regeneration

Zeolite exhausted with NH_3 was regenerated by feeding a solution 0.5 N or 0.1 N HCl. Before washing the column with HCl, 500 ml MQ was passed through the column to remove excess NH_4Cl in the column. For HCl, regeneration fresh columns were prepared as mentioned in Section 9.4.3.2.

The desired volume of sample was passed through newly prepared column at the flow rate of 15 ml/minute. First, 500 ml effluent was discarded to remove MQ water in the column. Then, effluent from the column was collected at the regular volume interval of 250 ml to measure the concentration of NH_3 at 250, 500, 750, 1000, 1250, 1500, 1750, 2000, 2250, 2500, 2750, 3000, 3250, 3500 & 3750 ml. In this experiment, all the effluent was stored. For example: NH_3 concentration in 250 ml was tested from bulk 250ml unlike in previous experiments. In addition, the actual time at which each effluent was collected was recorded simultaneously. NH_3 concentrations in collected samples were analyzed using an ammonia electrode as described in Section 9.2.5.

After passing predefined volume of sample, 2L of DI was passed through the column at the flow rate of 10 ml/minute to determine if DI water could contribute to the regeneration and minimize acid addition. NH_3 concentration in the effluent was measured at a regular interval of 250 ml. Then the column was washed with 0.5M HCL at the flow rate of 10 ml/minute. First 250 ml of sample was discarded since it might be diluted with MQ. The effluent from the column was collected at the regular volume interval of 250 ml to measure the concentration of NH_3 at 250, 500, 750, 1000, 1250, 1500, 1750, 2000, 2250, 2500, 2750, 3000, 3250, 3500, 3750 & 4000 ml. In this experiment, all the effluent was stored. The NH_3 concentrations in collected samples were analyzed using NH_3 electrode as described in Section 9.2.5.

After 0.5 M HCl wash, 250 ml DI was passed through the column to remove excess HCl and 4 L of sample was passed through the column. Similarly, 0.1 N HCl regeneration was carried out in the same manner as mentioned in Section 9.5.2. All the collected samples in the regeneration process were filtered through 0.45 μm white man filter and stored in -4°C until further use.

HCl regeneration process was repeated using different procedures but all the methods gave similar results. Hence, we stopped them all after 1st regeneration.

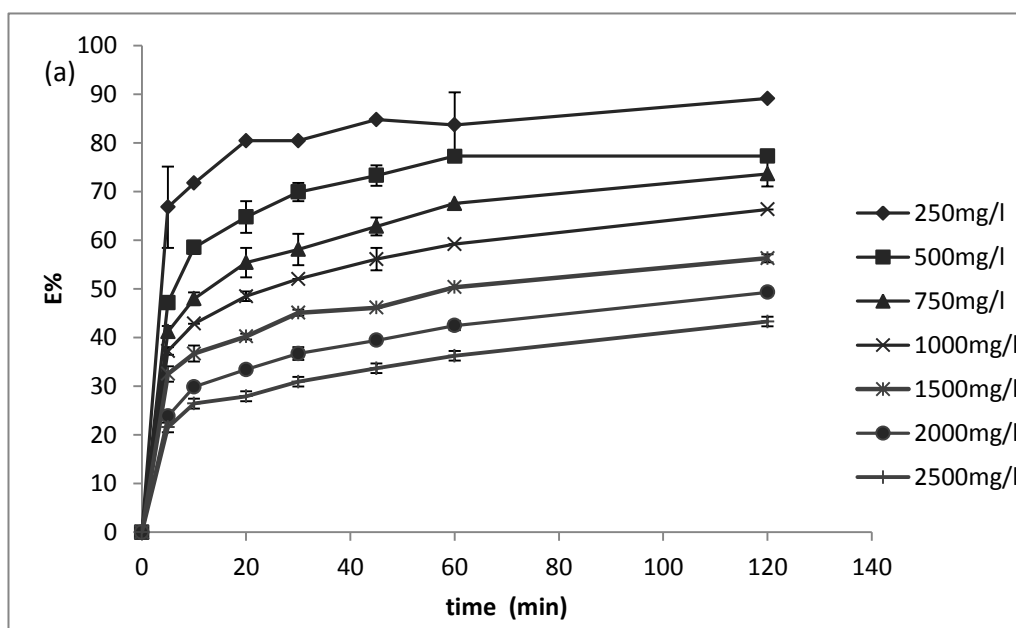
10. RESULTS AND DISCUSSION

10.1 Batch Study

Batch experiment was performed to study the effect of particle size, pH, NH_4^+ loads, TS, and contact time on NH_4^+ E% of zeolite. The data obtained from batch experiments were used to study equilibrium and kinetic models.

10.1.1 Effect of particle size and contact time

The effect of particle size and contact time on removal of $\text{NH}_4\text{-N}$ was studied with zeolite particle sizes 0.2-0.5 mm and 0.6-2.0 mm at different initial concentrations of $\text{NH}_4\text{-N}$ (250, 500, 750, 1000, 1500, 2000 and 2500 mg/l) ranging between 0 to 120 minutes are shown in Figure 24. From Figure 24, it is clear that $\text{NH}_4\text{-N}$ removal E% increased with decrease in particle size and increase in contact time. The removal rate was rapid at the initial contact time and maximum removal occurred within the first 10 minutes of contact time in both the zeolite type depending on the initial NH_4^+ concentration. This is because at the beginning of the experiment, there are large numbers of unoccupied sites in the adsorbent (Zhao et al, 2010; Du et al, 2005, Widisatuti et al, 2011), and fast diffusion onto available adsorbing sites (Huang et al, 2010; Karadag et al, 2006).



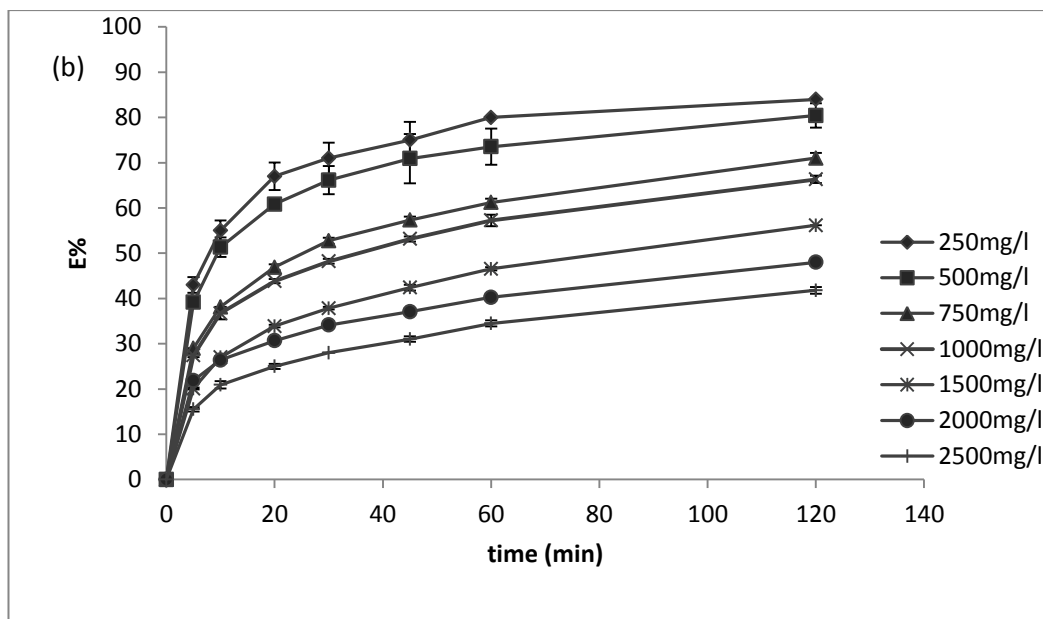


Figure 24: Effect of contact time on the removal of NH_4^+ (pH: 7.0 ± 0.5 ; contact time: 120 minutes; adsorbent dosage: 50g; sample volume: 500 ml): (a) 0.2-0.5 mm and (b) 0.6-2.0 mm; [SD: 1- 3 %]

The maximum and minimum $\text{NH}_4\text{-N}$ removal was observed with the lowest (250 mg/l) and the highest (2500 mg/l) concentrations of NH_4^+ , respectively on both zeolite types. At initial concentration of 250 mg/l, at the first 5 minutes, E% of 0.2-0.5 mm and 0.6-2.0 mm zeolite particles were 67% and 43%, respectively with the difference of 24% in E%. Similarly at 10 minutes of experimental time, E% were 72% and 55% for zeolite particles 0.2-0.5 mm and 0.6-2.0 mm, respectively with E% difference of 17%. For initial concentrations 500, 750, 1000 and 1500 mg/l, the first 10 minutes had E% difference of $10 \pm 3\%$ between both zeolite types. But, with initial concentration 2000 and 2500 mg/l the difference between E% was very minimal ($4 \pm 2\%$) in the initial first 10 minutes of the experiment. However, the difference between E% decreased with the increase in contact time for all the concentrations in both the zeolite types. Also, difference between E% of zeolites 0.2-0.5 mm and 0.6-2.0 mm decreased with the increase in concentrations and at 120 minutes the difference was negligible. This is as expected since the higher initial NH_4^+ concentrations will saturate the zeolite faster than lower concentration. Also, with increase contact time, NH_4^+ removal rate decreases as all the adsorption site are almost occupied and approaches to zero when it reached equilibrium (Widiastuti et al, 2011).

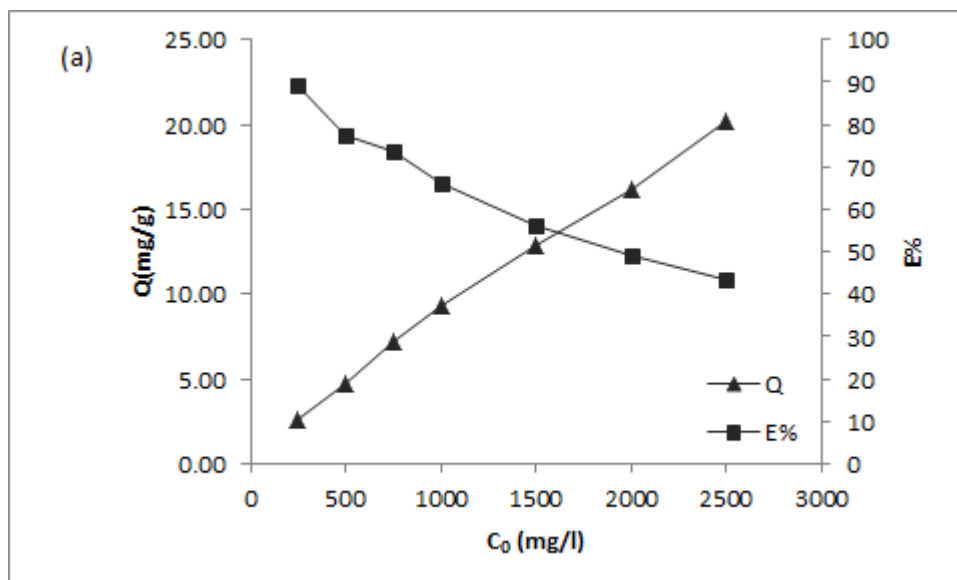
Cations in small zeolite particles are exchanged easily with cations in aqueous solutions as a result of high mass transfer (Hedström, 2001; Huang et al, 2010; Wen et al, 2006; Kucic et al, 2012), greater specific surface area (Huang et al, 2010; Malakian et al, 2011; Wang et al, 2006; Langwaldt, 2008), and shorter diffusion paths (Kammerer et al, 2011). Total surface area of zeolite is made of external and internal surface areas. When the material is crushed into smaller particle size, the external surface area is increased with minor change in internal surface area. Therefore, specific surface area is

directly related to external surface area. Specific surface area can be expressed as the multiple of the outer surface of the adsorbent (Kammerer et al, 2011). Hence a decrease in particle size exposes larger external surface area to NH_4^+ ions and thus higher adsorption capacity. Similarly with a decrease in particle size a mass exchange rate had increased as it shortens diffusion paths.

Similar results were observed by Zhao et al, 2010 and Karadag et al, 2006. Karadag et al, 2006 have reported more than 70% of NH_4^+ uptake within the first 10 minutes of contact time. Widiastuti et al, 2011, and Du et al, 2005 reported that NH_3 uptake by zeolite occurred at initial 15 minutes. This finding has been supported by results of other researchers (Karadag et al, 2006; Zhao et al, 2010, Saltali et al, 2007).

10.1.2 Effect of initial ammonium concentration

Figure 25 and Figure 26 depict the experimental results for NH_4^+ adsorption and E% for various initial NH_4^+ concentrations in the solutions. From experimental results, it can be seen that Q of zeolite increased with an increase in initial concentration of NH_4^+ in both zeolite types (Figure 25(a) and Figure 26 (a)). Both zeolite types showed the similar pattern of Q as maximum adsorption was at concentration of 2500 mg/l and minimum at concentration of 250 mg/l. The adsorption rate was faster at the first 10 minutes and it slowed down with an increase in contact time for all the concentrations (Figure 25 (b) and Figure 26 (b)). At the initial concentrations 250 mg/l, the adsorption rate was constant after 20 minutes of the experiment for zeolite particle 0.2-0.5 mm (Figure 25 (b)) whereas for zeolite particle 0.6-2.0 mm, it reached at constant adsorption rate after 30 minutes (Figure 26 (b)).



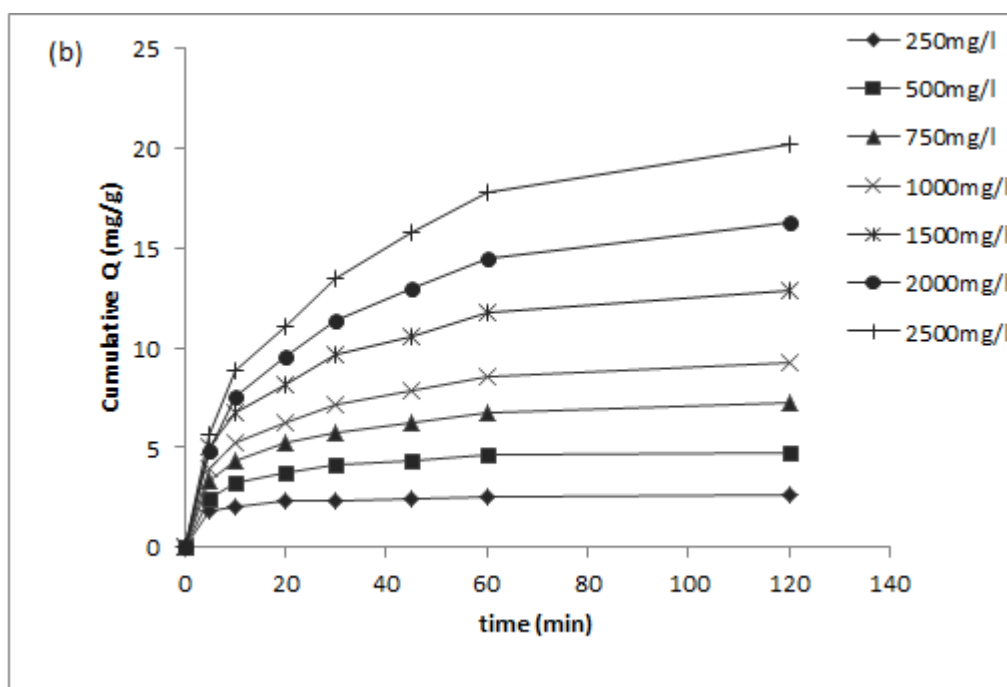
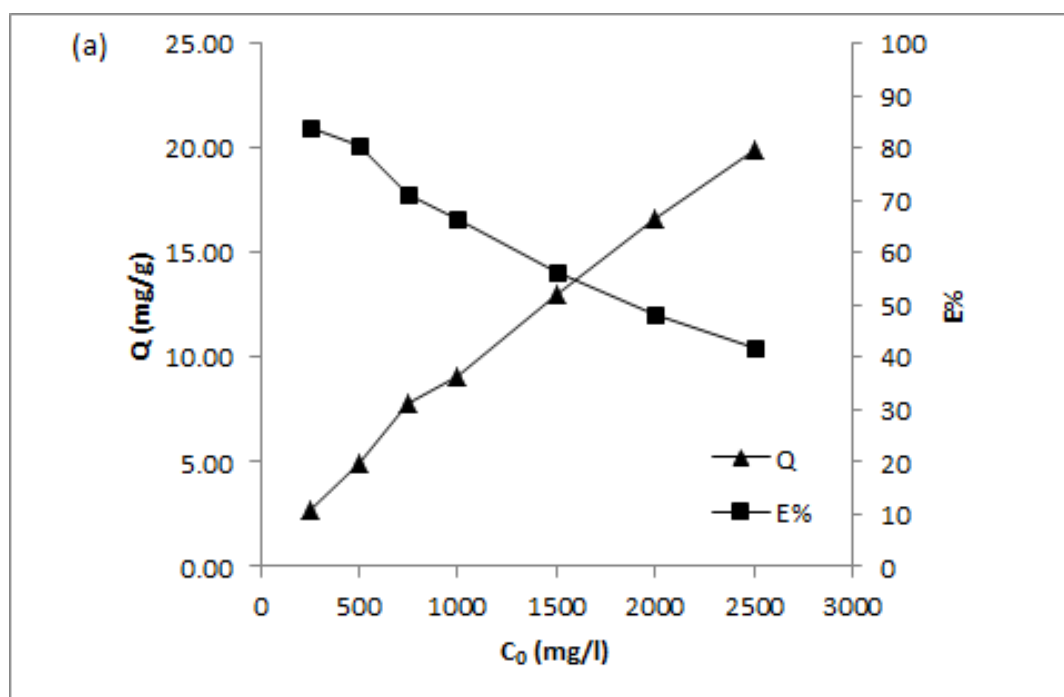


Figure 25: Effect of initial NH_4^+ concentration on zeolite (particle size: 0.2-0.5 mm; pH: 7.0 ± 0.5 ; contact time: 120 minutes; adsorbent dosage: 50 g; sample volume: 500 ml)



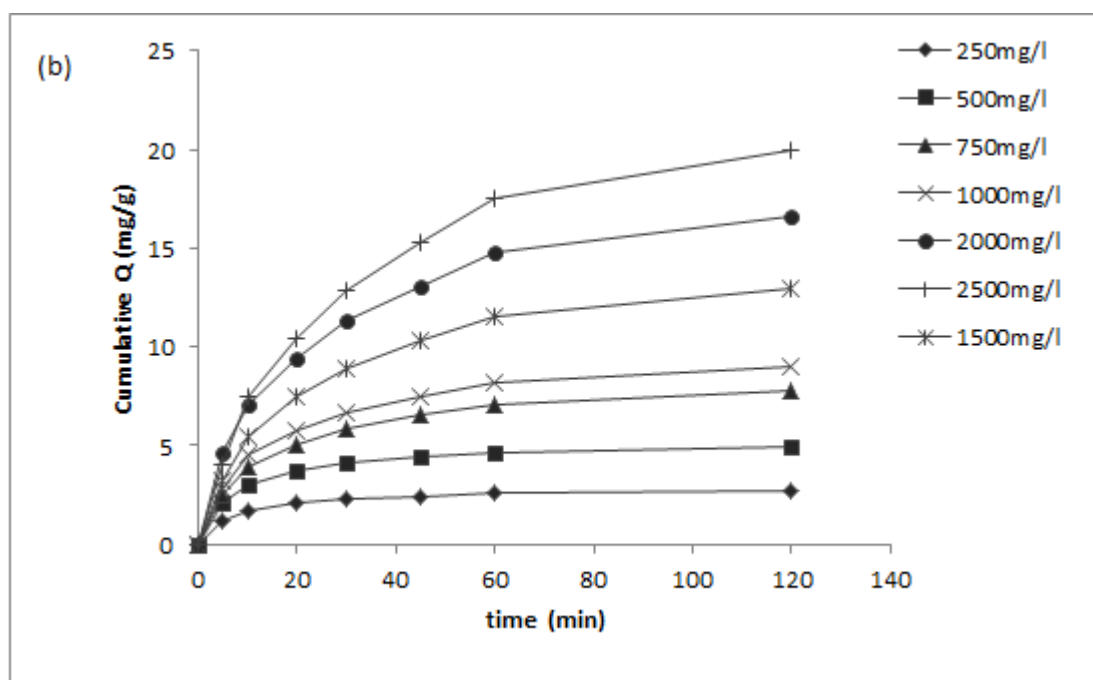


Figure 26: Effect of initial NH_4^+ concentration on zeolite (particle size: 0.6-2.0 mm; pH: 7.0 ± 0.5 ; contact time: 120 minutes; adsorbent dosage: 50 g; sample volume: 500ml)

At the first 5, 10 and 20 minutes, 0.2-0.5 mm showed higher adsorption capacity than 0.6-2.0 mm zeolite particles in all the concentrations. But at 120 minutes, both zeolite types showed the same amount of Q with respect to concentrations.

The uptake rate of NH_3 increased with the increase in initial NH_4^+ concentration. It is because exchange capacity of NH_4^+ increased with an increase in the initial concentration of NH_4^+ as the result of a higher concentration gradient. The difference in concentration gradient provides required driving force for NH_4^+ ions to replace other cations in the zeolite framework (Erdogan & UIKu, 2011; Zhao et al, 2010). The driving force is the concentration of the solution and it helps to overcome the barrier between solution and zeolite phase. Hence, it is always proportional to the rate of sorption to the surface by area (Karadag et al, 2006). Also in NH_4^+ IE cations are exchanged in both the internal and external surfaces of zeolites. Increase concentration of NH_4^+ helps NH_4^+ ions to travel from an external surface to the internal micropores of zeolite within the given time frame (Du et al, 2005; Widiastuti et al, 2011). Hence, NH_3 adsorption capacity increased with an increase in initial concentration of NH_4^+ in the solution (Du et al, 2005; Zhao et al, 2010; Malekain et al, 2011; Widiastuti et al, 2011). However, E% decreased with an increase in initial concentration of NH_4^+ in solution due to saturation of the adsorbent (Zhao et al, 2010; Malekain et al, 2011).

10.1.3 Effect of pH

The effect of pH on the removal of $\text{NH}_4\text{-N}$ was studied with zeolite 0.2-0.5 mm at different pH ranges from 6 to 8.5 as shown in Figure 27. Different pH showed similar pattern of E% with average of 58% removal and 13.77 mg/g adsorption capacity in 2

hours contact time. The maximum $\text{NH}_4\text{-N}$ removal was observed at pH 6 with removal of 60%. From the experimental results, it was clear that pH had minimum effect on the NH_4^+ exchange at the pH ranges 6.0-8.5. The removal efficiency here is lower compared to the efficiency in the previous experiments ($E\% = 89$, observed with 250 mg/l initial NH_4^+ concentration at pH 7.0), that is because in this experiment the effect of pH on NH_4^+ removal by zeolite was studied at higher NH_4^+ load (1500 mg/l) to simulate real NH_4^+ concentration of bioslurry.

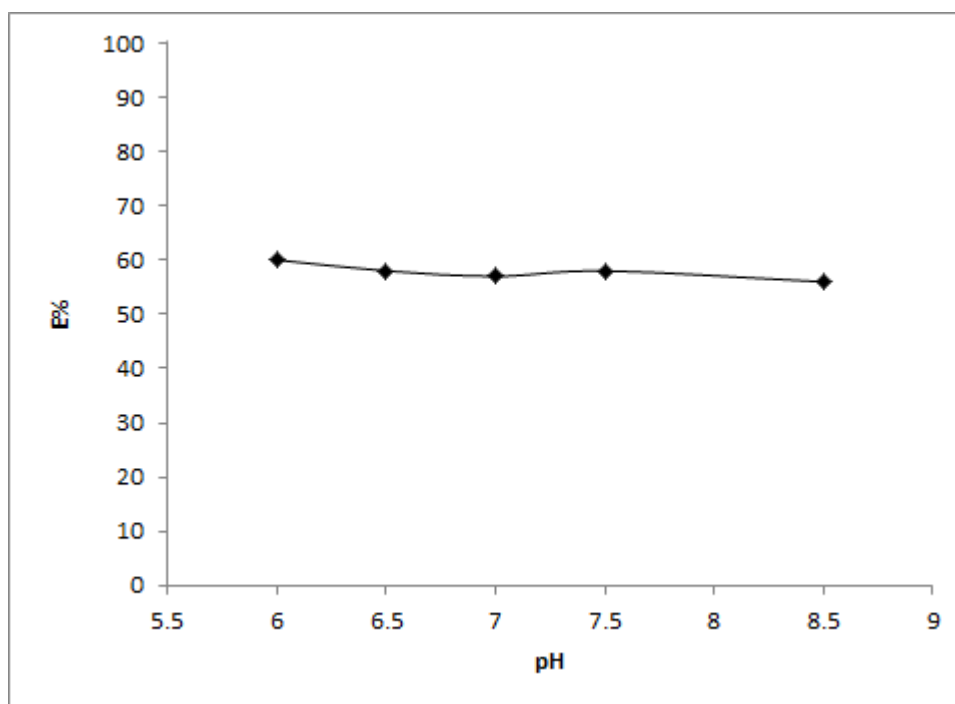


Figure 27: Effect of pH on NH_4^+ removal (particle size: 0.2-0.5 mm; initial NH_4^+ concentration: 1500 mg/L; contact time: 120 minutes; adsorbent dosage: 50 g; sample volume: 500 ml); [SD: 1%]

Since cation exchange take place only by means of NH_4^+ ion (Burgess et al, 2004), the exchange rate should be greater at lower pH according to equilibrium reaction (Figure 2). Even batch experiment results at different pH (2-12) and pH (4-10) by Englert & Rubio, 2005 and Du et al, 2005 respectively showed that the optimal pH for NH_3 removal is pH 6, but pH above and below pH 6 showed a decrease in NH_3 removal. At alkaline pH, E% decreased sharply due to the partial dissolution of zeolite (Huang et al, 2010) and transformation of ionized NH_4^+ to non-ionised $\text{NH}_{3(\text{aq})}$ which is not favorable for surface adsorption of zeolite (Zhao et al, 2010; Thornton et al, 2007; Saltali et al, 2007). Similarly, at lower pH, NH_4^+ has to compete with H^+ ions (Erdogan & Ulku, 2011; Hedström, 2001; Huang et al, 2010; Thornton et al, 2007) and H_3O^+ ions (Li et al, 2011) for the exchange sites. Besides at very low pH (pH 2), zeolites tend to dissolve (Leyva-Ramos et al, 2004; Widiastuti et al, 2011). However, optimal pH value near neutral range was obtained in many studies (Maranon et al, 2006; Karadag et al, 2007; Thornton et al, 2007).

10.1.4 Effect of TS

NH_4^+ removal capacity of zeolite decreased with an increase in TS (Figure 28). The zeolite particle 0.2-0.5 mm and 0.6-2.0 mm showed similar amount of E% $72 \pm 2\%$ and $70 \pm 2\%$, respectively for 0, 5, 7.5 and 10 %. However, 0.2-0.5 mm zeolite particle was slightly better than 0.6-2.0 mm in NH_4^+ removal. In case of 0.2-0.5 mm zeolite particle size E% decrease gradually with an increase in TS% and decreased sharply at TS 75% and 100% to E% 32% (Figure 28 (a)). However, zeolite particle 0.6-2.0 mm showed a gradual decrease in E% from 71% to 59% (Figure 28 (b)).

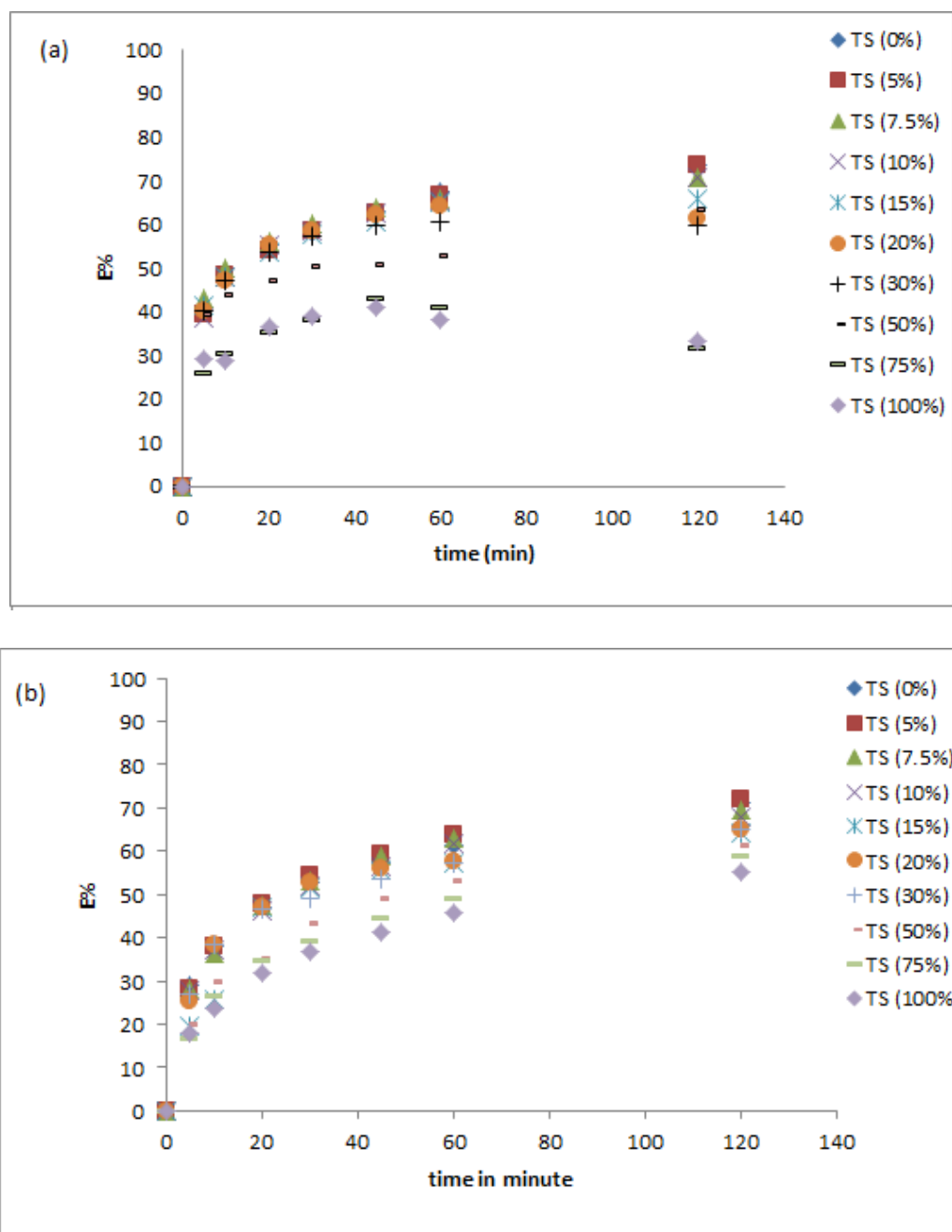


Figure 28: Effect of TS on NH_4^+ adsorption ((particle size: 0.2-0.5 mm; pH: 7.2 ± 0.3 ; initial NH_4^+ concentration: 750 mg/l; contact time: 120 minutes; adsorbent dosage: 50 g; sample volume: 500 ml): (a) 0.2-0.5 mm and (b) 0.6-2.0 mm; [SD: $\pm 2\%$])

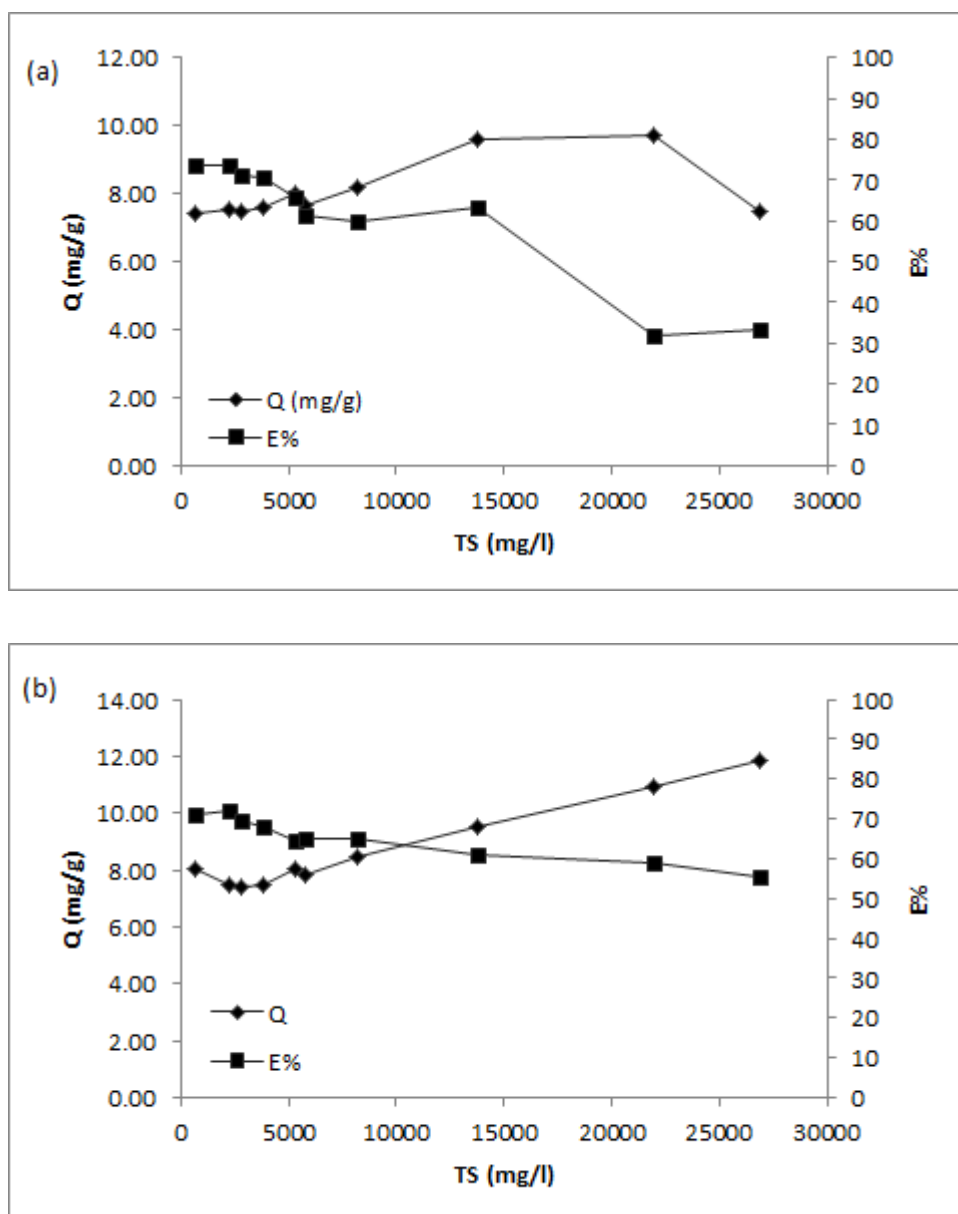


Figure 29: Effect of TS concentration on NH_3 removal: (a) 0.2-0.5 mm and (b) 0.6-2.0 mm

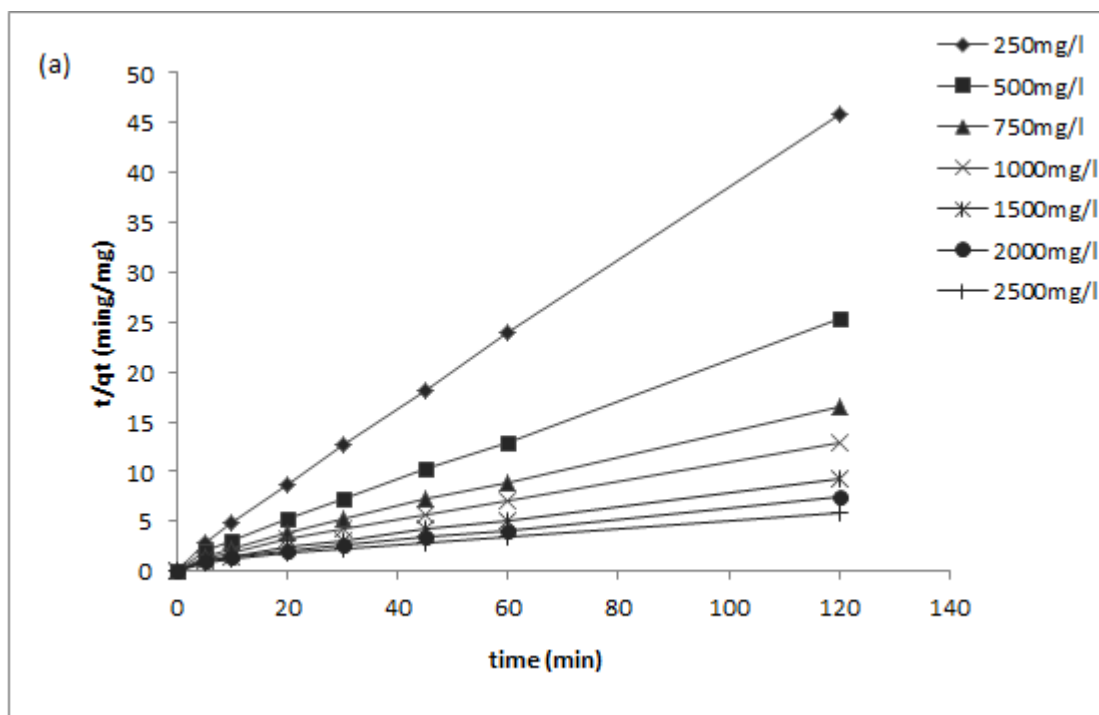
From Figure 29 (a), Q of zeolite particles 0.2-0.5 mm were more or less same with an average of 7.6 mg/g until 5800 mg/l TS concentration. Q of TS increased gradually from 5800 mg/l to 13700 mg/l TS concentration. Then after, Q was almost the same till 21900 mg/L TS concentration and it dropped to 7.46mg/g at 26900 mg/l TS concentration. The maximum and minimum Q was observed at 21900 and 640 mg/l TS concentrations.

From Figure 29 (b), Q of zeolite particles 0.6-2.0 mm dropped from 8.01 mg/g to 7.51 mg/g at 2240 mg/l TS concentration. Then after, Q was more or less same with an average of 7.7 mg/g till 5800 mg/l TS concentration. After 5800 mg/l TS concentration, there was steady increase in Q till the end of the experiment. The maximum Q was observed at highest TS concentration (26900 mg/l).

The difference in adsorption phenomenon between these zeolite particles with increasing concentration of TS might be the result of experimental condition. While conducting experiment, it was difficult to separate between supernatant and settled sludge while withdrawing samples with an increase in TS concentration in 0.2-0.5 mm zeolite particles. The sharp decrease in E% with zeolite particles 0.2-0.5 mm might be due to smaller void space compared to 0.6-2.0 mm as a result solids tend to block the flow and interfere with the IE of smaller zeolite. There is no literature available on solids effect on NH_4^+ exchange capacity of the zeolite.

10.2 Kinetic studies

Adsorption kinetics is required for selecting optimal operational condition of wastewater treatment plant. To study the adsorption mechanism of NH_4^+ ion uptake onto both zeolite types, pseudo first and second order kinetics were studied at various NH_4^+ concentrations (250, 500, 750, 1000, 1500, 2000 and 2500 mg/l). The pseudo-first order model did not fit perfectly to our results. To test the pseudo-second order model t/q_t was plotted against t , which gave a linear relationship as shown in Figure 30. The linear relationship values for K_2 , q_e , and R^2 were calculated from the slope and intercept of the straight-line plots of t/q_t versus t and are depicted in Table 11.



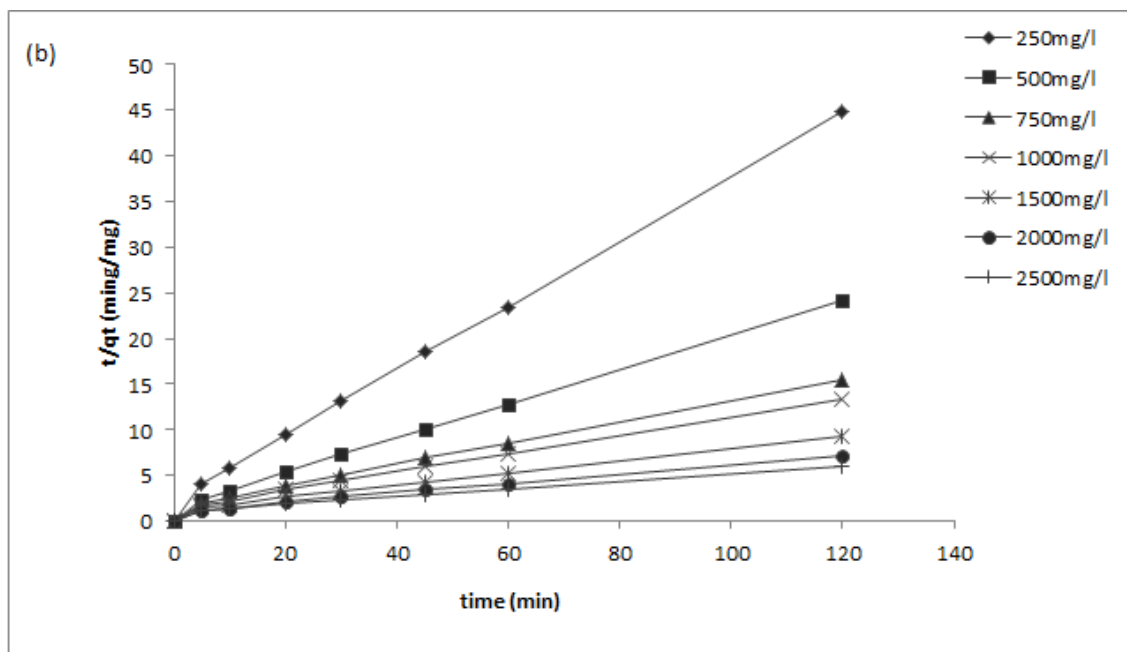


Figure 30: Pseudo second order sorption kinetics of zeolite particles (a) 0.2-0.5 mm and (b) 0.6-2.0 mm at various initial concentrations

The pseudo-second order rate constant (K_2) and q_e values increased with an increase in initial concentrations in both the zeolite types. K_2 values ranged between 2.64 to 21.79 g/(mg.min) and 2.77 to 22.22 g/(mg.min) for 0.2-0.5 mm and 0.6-2.0 mm zeolite types respectively (Table 11). This indicates that the higher initial concentrations need a longer time period to reach equilibrium. Further, in all the concentrations, 0.2-0.5 mm zeolite particle reach equilibrium faster than 0.6-2.0 mm zeolite particles as K_2 values were smaller for 0.2-0.5 mm. Similarly, zeolite particles 0.2-0.5 mm and 0.6-2.0 mm has q_e ranging between 22-33 and 11- 26 mg/g respectively which means Q of 0.2-0.5 mm zeolite is higher compare with another one. R^2 for zeolite particles 0.2-0.5 mm and 0.6-2.0 mm decreased with an increase in initial concentration and ranged between 1 to 0.98 and 1 to 0.96 respectively. The difference between R^2 for all the concentrations is negligible. Therefore, high value of R^2 confirmed that adsorption of NH_4^+ ion on zeolite followed the pseudo-second order kinetic model. Erdogen & Ulku, 2011 investigated kinetic parameters for NH_4^+ sorption by zeolite and reported that pseudo second order kinetic model fitted experimental data.

Table 11: Values for the pseudo-second order constants determined from Figure 30

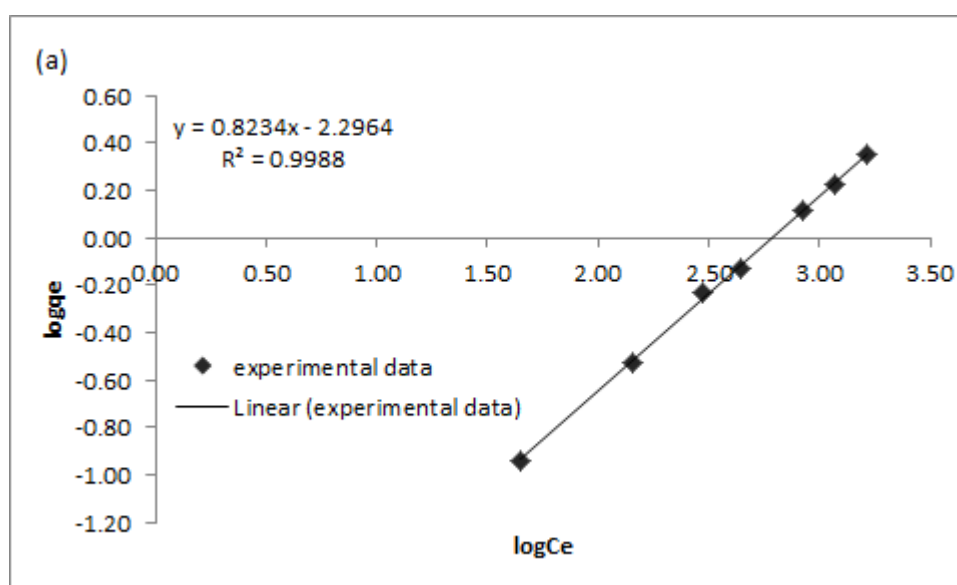
Zeolite particles	C0	K ₂	q _e	R ²
	mg/l	g/(mg. min)	mg/g	
0.2-0.5mm	250	2.64	22	1
	500	4.89	23	1
	750	7.5	23	0.99
	1000	9.64	26	0.99
	1500	13.51	30	0.99
	2000	17.36	30	0.98
	2500	21.79	33	0.98
0.6-2.0mm	250	2.77	11	1
	500	5.15	17	1
	750	8.21	18	0.99
	1000	9.58	19	0.99
	1500	14.18	21	0.98
	2000	17.99	27	0.98
	2500	22.22	26	0.96

10.3 Isotherm studies

Isotherm studies is necessary for insight into the adsorption mechanism pathways, adsorbent capacity, surface properties, and a degree of affinity to the adsorbent and an effective design of the adsorption system (Foo & Hameed, 2010). Isotherm study was carried out using Langmuir and Freundlich equilibrium isotherm.

10.3.1 Freundlich isotherm

Freundlich equilibrium isotherm data for NH_4^+ adsorption on the zeolite particles (0.2-0.5 mm and 0.6-2.0 mm) is shown in Figure 31 where $\text{Log}q_e$ was plotted against $\text{log}C_e$.



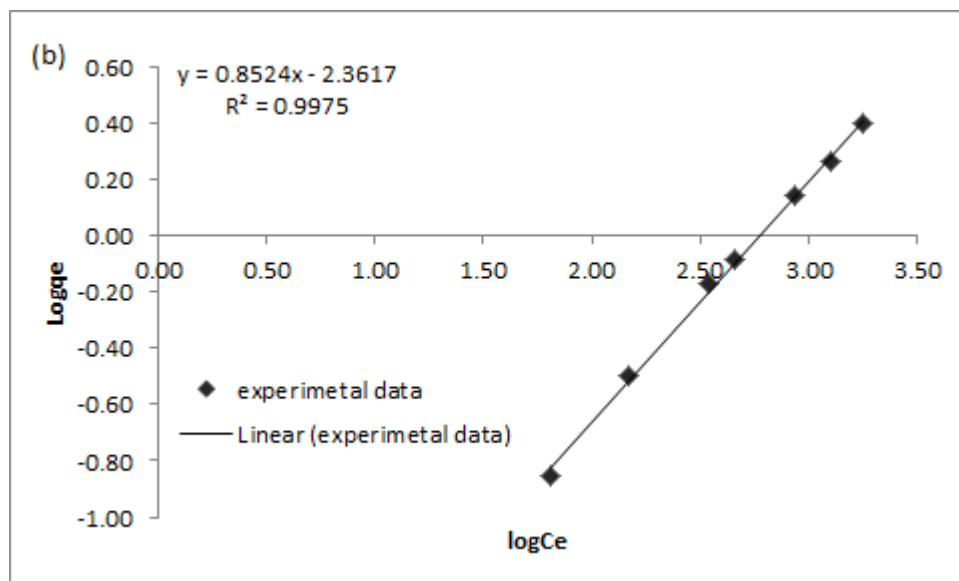


Figure 31: Linear plot of Freundlich isotherm model for NH_4^+ adsorption on zeolite: (a) 0.2-0.5 mm and (b) 0.6-2.0 mm

The experimental data fits Freundlich model as R^2 for both zeolite types 0.2-0.5mm and 0.6-2.0 mm was similar 0.999 and 0.998 respectively. The values for the coefficient K and $1/n$ were calculated from a linear plot of experimental data (Table 12). Zeolite particles 0.2-0.5 mm and 0.6-2.0 mm had K_f values 0.005 and 0.004 respectively.

Table 12: Values for Freundlich coefficients determined from Figure 31

zeolite particles	Freundlich parameter			q_e (mg/g)	R^2
	K_f	$1/n$	n		
0.2-0.5mm	0.005	0.823	1.22	1.053	0.999
0.6-2.0mm	0.004	0.852	1.17	0.901	0.998

In Freundlich isotherm, the dimensionless constant $1/n$ indicates whether the experimental conditions are favorable or unfavorable for adsorption experiment. If $n > 1$, experimental conditions are favorable for experiment (Kucic et al, 2012; Huo et al, 2012). In our experiment, we obtain $n > 1$ for both the zeolite types which mean our experimental conditions were suitable for NH_4^+ adsorption. Similarly, Freundlich constant K_f is related to the adsorption capacity of zeolite, from experimental values, it was clear from experimental data that 0.2-0.5 mm had higher affinity for NH_4^+ , and had better q_e compared with 0.6-2.0 mm zeolite particles.

10.3.2 Langmuir isotherm

Langmuir equilibrium isotherm data for NH_4^+ adsorption on the zeolite particles (0.2-0.5mm and 0.6-2.0mm) was achieved by plotted C_e against C_e/q_e (Figure 32). The values for Langmuir parameter K_L and q_{\max} were obtained from slope and the intercept of the graph.

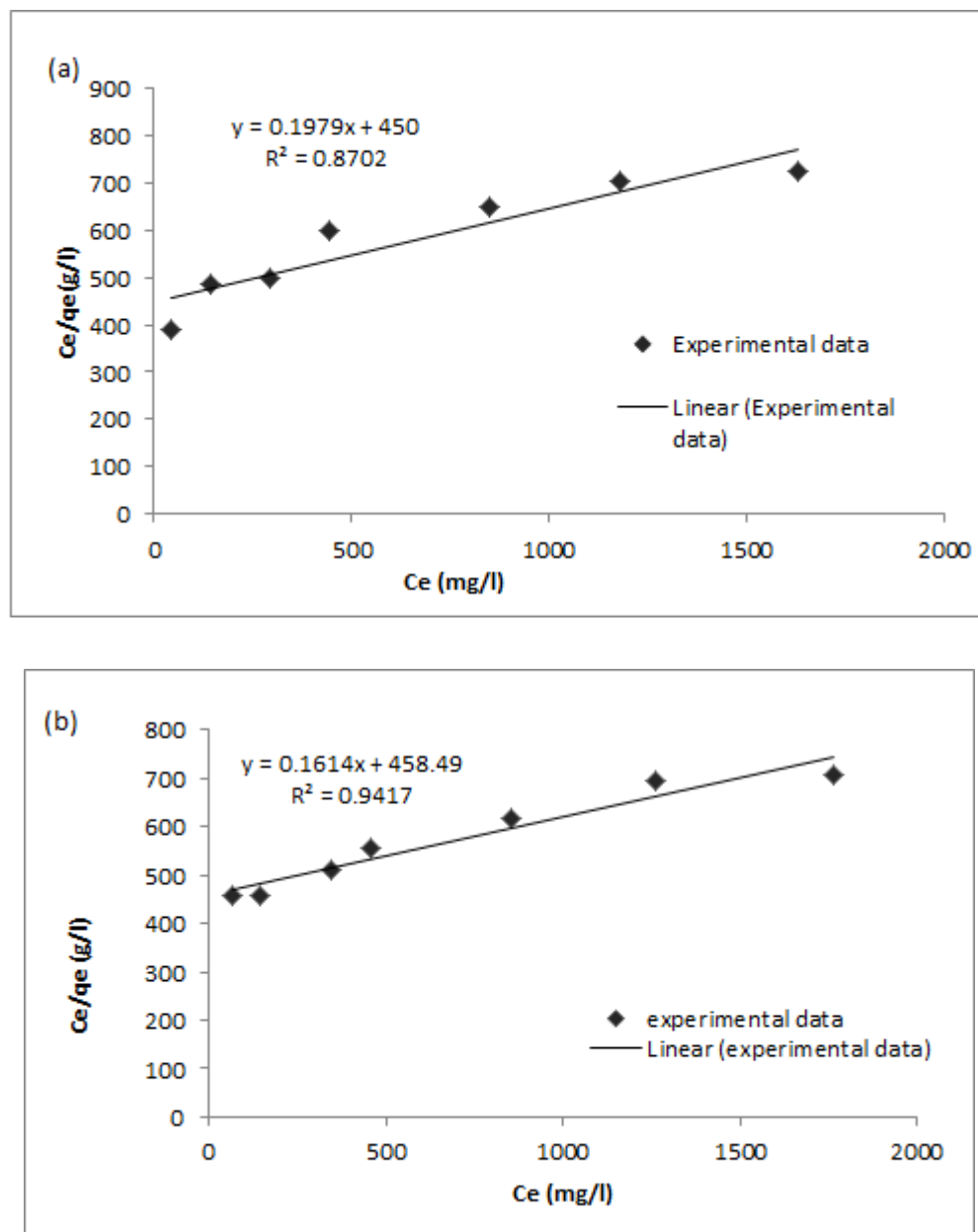


Figure 32: Linear plot of Langmuir isotherm of NH_4^+ adsorption on zeolite (a) 0.2-0.5 mm, and (b) 0.6-2.0 mm

The experimental data fits Langmuir model as R^2 values of the plot for 0.2-0.5 mm and 0.6-2.0 mm were found to 0.870 & 0.941 respectively from the linear plot. The value for Langmuir parameter K_L and q_{\max} was obtained from a linear plot (Figure 32). The maximum adsorption capacity and the adsorption energy coefficient are enlisted in Table 13.

Table 13: Values for Langmuir coefficients determined from Figure 32

zeolite particles	Langmuir parameter		q_e (mg/g)	R^2
	K_L (mg/L)	q_{\max} (mg/g)		
0.2-0.5mm	0.0004	5.053	1.05	0.870
0.6-2.0mm	0.0004	6.196	1.14	0.941

The variation of a separation factor (R_L) with initial concentration is shown in Figure 33. The R_L values were in the range $0 < R_L < 1$ in both the zeolite types which indicated NH_4^+ exchange with zeolite was favorable for zeolite from Zeocem®. The R_L value was decreasing with an increase in concentration which indicates NH_4^+ exchange is less favorable at high initial concentration.

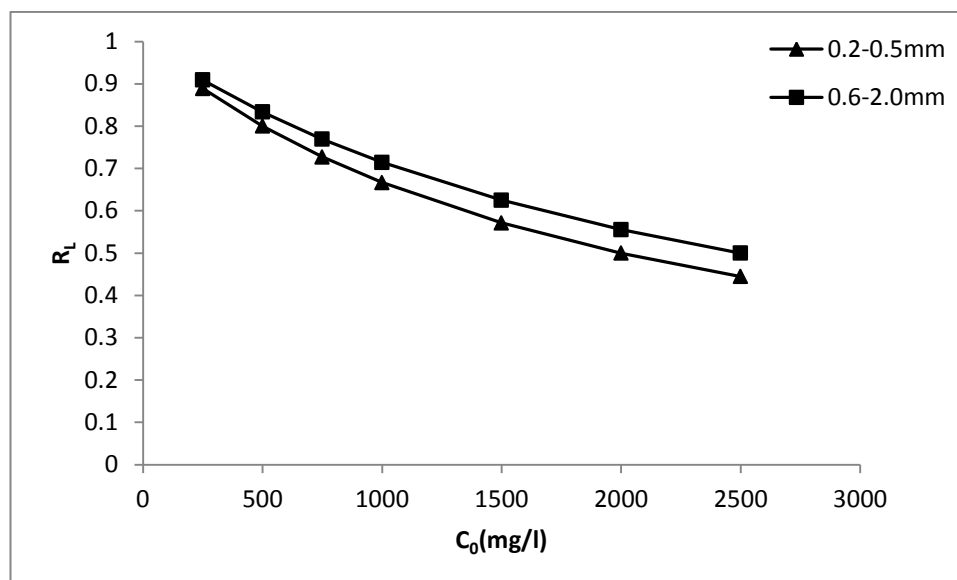


Figure 33: Variation of separation factor (R_L) as a function of initial concentration of NH_4^+ ion

10.4 Column study

Column experiments are needed to learn how the system will function in natural environment. In column experiment, the effect of flow rate, pH and regeneration capacity of zeolite was studied using both the zeolite types 0.2-0.5 mm and 0.6-2.0 mm.

10.4.1 Effect of flow rate

$\text{NH}_3\text{-N}$ removal by zeolite was studied at five different flow rates (10, 20, 30, 40 and 50 ml/min). The experimental results for zeolite particle size (0.2-0.5 mm and 0.6-2.0 mm) are shown in Figure 34. From these results, it can be said that higher the flow rate, lower the E% in both the zeolites that is 50 ml/min flow rate showed minimum and 10 ml/min showed maximum E%. In all the flow rates, $\text{NH}_3\text{-N}$ E% was higher with 0.2-0.5 mm particle size zeolite.

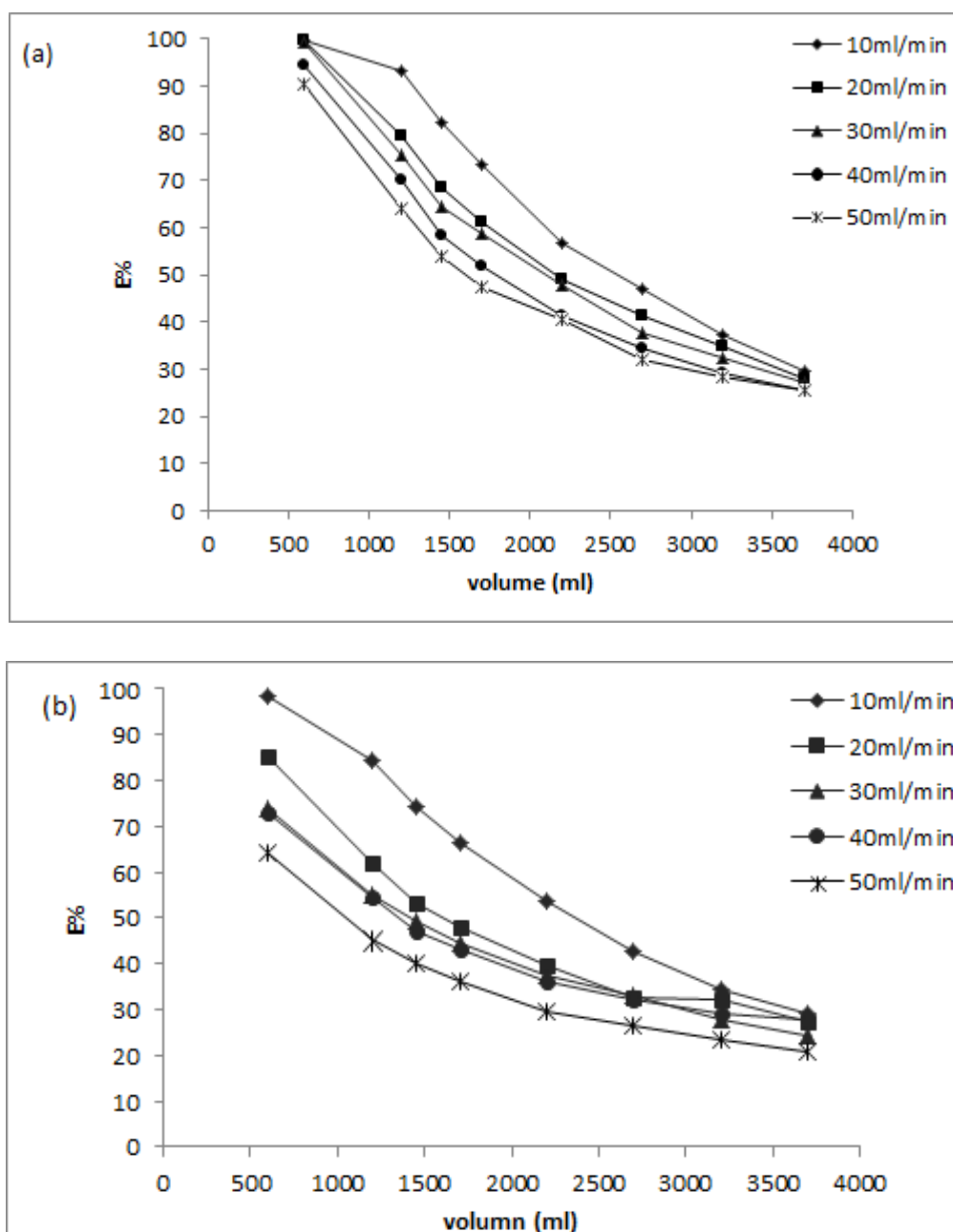


Figure 34: Effect of flow rate (initial NH_4^+ concentration: 1500 mg/L; pH: 7.0 ± 0.5 ; adsorbent dosage: 300 g; sample volume: 4000 ml): (a) 0.2-0.5 mm and (b) 0.6-2.0 mm

$\text{NH}_3\text{-N}$ Q at different flow rate was calculated using equation 45 is shown in Table 14. Q of 0.2-0.5 mm zeolite particle in all the flow rates was higher as compare with 0.6-2.0 mm. The Q rate decreased with increased in flow rates. The maximum Q was observed at 10 ml/minute flow rate where 0.2-0.5mm and 0.6-2.0mm showed Q of 7.20 mg/g and 6.02 mg/g respectively.

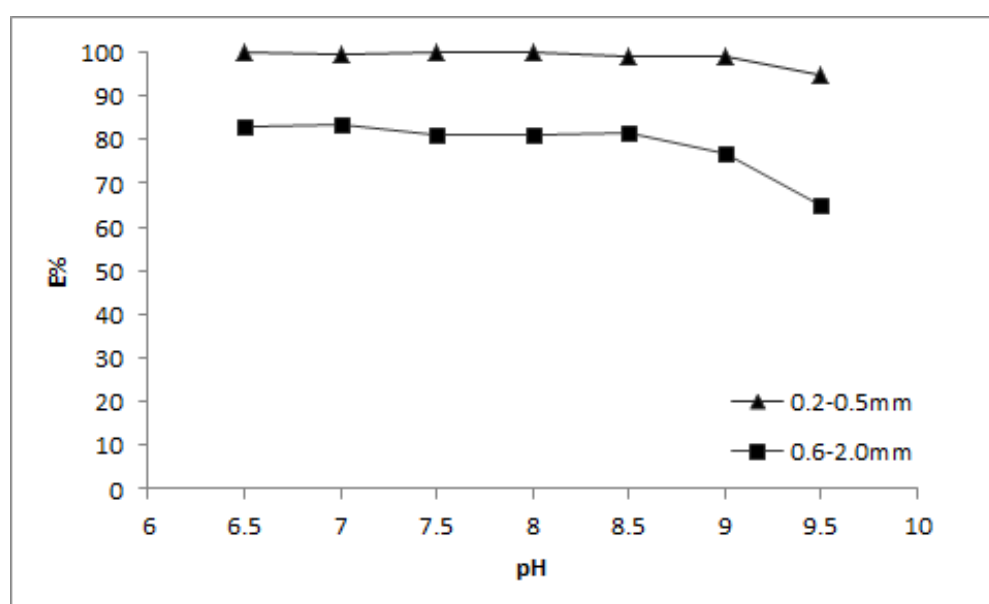
Table 14: Adsorption capacity of zeolite particles at different flow rate

Flow rate (ml/min)	Q (mg/g)	
	0.2-0.5mm	0.6-2.0mm
10	7.2	6.02
20	3.14	3.59
30	1.98	1.51
40	1.38	1.26
50	1.11	0.72

The E% and Q increased with a decreased flow rate. It was because a lower flow rate provided enough hydraulic retention time between the NH_4^+ ions solution and zeolite to bind to active sites (Cyrus & Reddy, 2011; Du et al, 2005) and for particle diffusion (Sprynskyy et al, 2005). Hence, higher amount of NH_4^+ removed by zeolite. Whereas in the case of higher flow rate, the contact time between solution and zeolite is less as a result less amount of NH_4^+ is removed by zeolite.

10.4.2 Effect of pH

Figure 35 represents experimental results for pH effect on the $\text{NH}_3\text{-N}$ removal by zeolite in column studies. Figure 35 (a), it was clear that E% was higher at all the pH ranges with 0.2-0.5 mm particle size zeolite. Similarly, it was observed that for zeolite with particle size 0.2-0.5 mm, at pH range of 6.5 to 9, $\text{NH}_3\text{-N}$ E% was nearly constant (100%) with an average Q of 3.28mg/g and at pH 9.5 the removal efficiency dropped slightly to 95% with Q 2.38 mg/g. Also, for zeolite with particle size 0.6-2.0 mm, at pH ranges of 6.5 to 8.5, E% was nearly constant (80%) with average Q 2.02 mg/g. At pH 9.0, it slightly decreased to 78% with Q 1.86 mg/g and at pH 9.5 it sharply decreased to 65% with Q 1.51 mg/g.



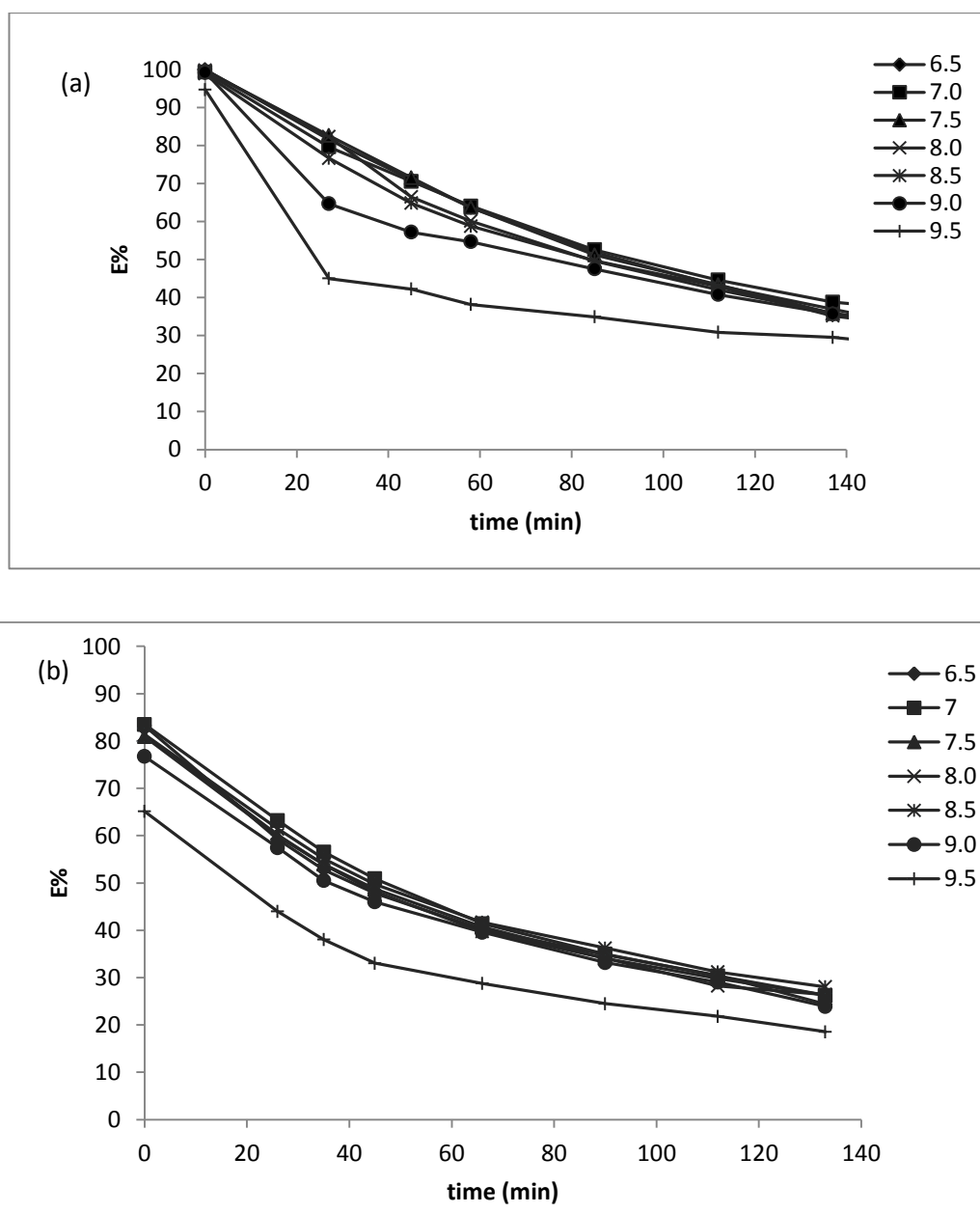


Figure 35: Effect of pH on NH_3 removal at different pH (initial NH_4^+ concentration: 1500 mg/L; flow rate: 25 ± 1 ml/minute; adsorbent dosage: 300 g; sample volume: 4000 ml): (a) 0.2-0.5 mm and (b) 0.6-2.0 mm

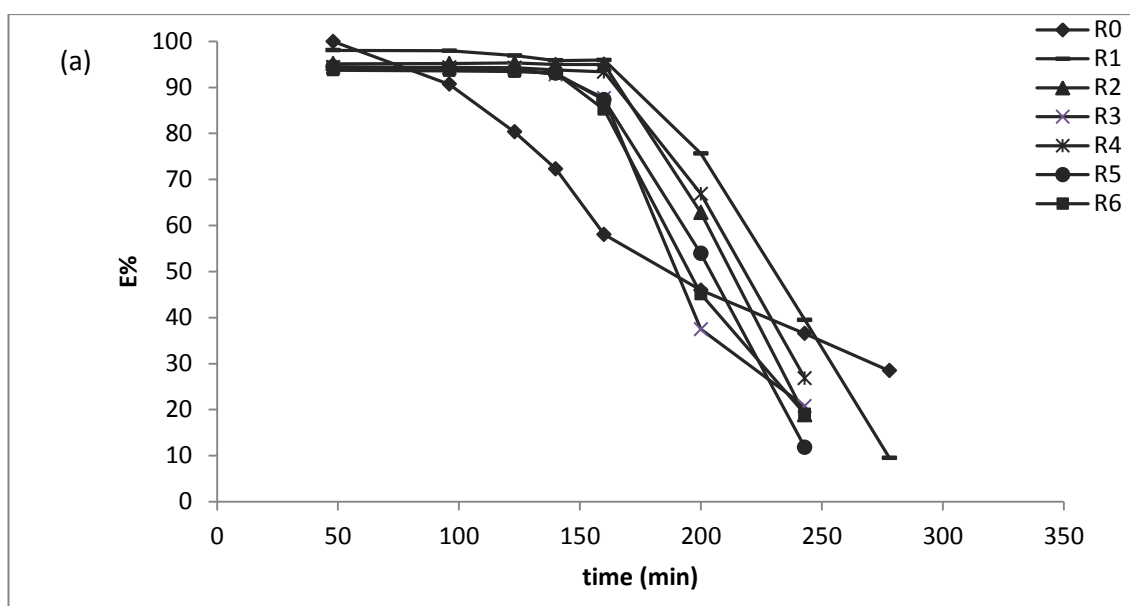
In Figure 35(b) and (c), for both types of zeolite, E% showed a gradual decrease in NH_3 -N removal with an increase in contact time at the pH range 6.5 to 9.0. But, at pH 9.5, there was a sharp decrease in E% for the first 30 minutes of the experiment and later E% decreased gradually with an increase in contact time. The steep reduction in NH_3 removal at alkali condition (pH > 9) could be due to formation of non-ionized $\text{NH}_{3(\text{aq})}$ and cations in zeolite can exchange only with NH_4^+ as a result at high pH minimal adsorption capacity was normal (Burgess et al, 2004). From the experimental data, it is clear that pH did not affect the performance of zeolite in removing NH_3 at experimental pH range, except for pH 9.5. The decrease in E% at pH 9.5 is due to low concentration of NH_4^+ at high pH.

10.4.3 Regeneration

Regeneration of NH_4^+ -zeolite is an important step in wastewater treatment. Regeneration is necessary for long term efficiency and cost reduction in wastewater treatment.

10.4.3.1 NaCl regeneration

Seven loading and six regeneration cycles were carried out in order to study the effect of regeneration in Q of zeolite (Figure 36). In this experiment, it was observed that $\text{NH}_3\text{-N}$ E% of zeolite increased after the first regeneration. When the regeneration cycle was repeated, $\text{NH}_3\text{-N}$ Q of zeolite remained constant in a subsequent loading process. It means during regeneration, Na^+ ions have activated the zeolite column by changing it into single ionic Na^+ forms.



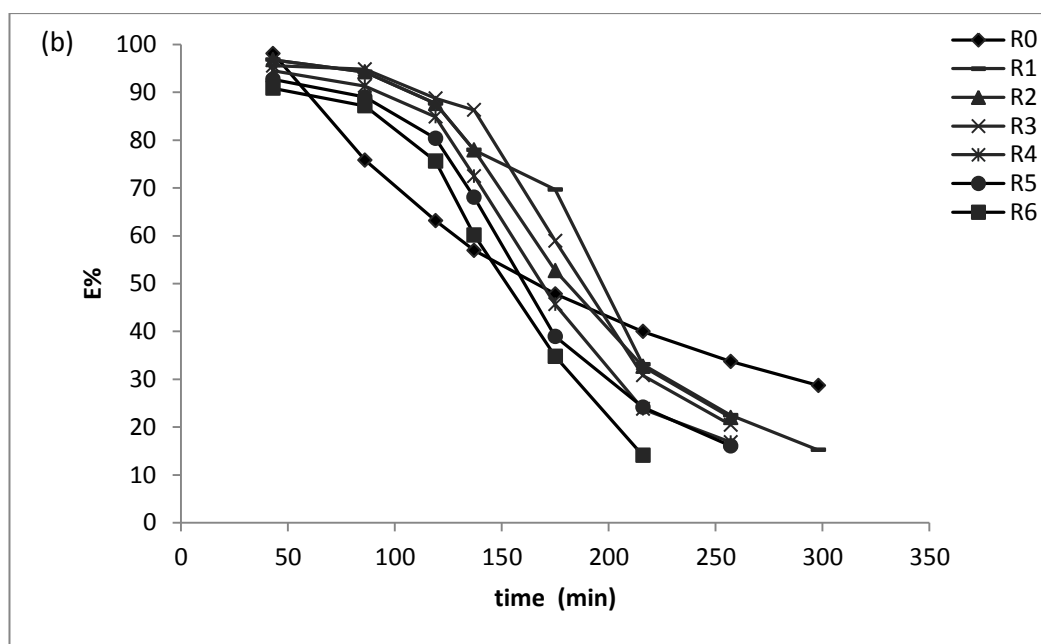


Figure 36: 0.5M NaCl regeneration (initial NH_4^+ concentration: 1500 mg/L; particle size: 0.2-0.5 mm, pH: 7.0 ± 0.1 ; flow rate: 15 ml/minute; adsorbent dosage: 300 g; sample volume: 4000 ml): (a) 0.2-0.5 mm and (b) 0.6-2.0 mm

From Figure 36 (a), for 0.2-0.5 mm particle size zeolite, in 1st run (R0), it was observed that the first 45 minutes had E% above 90% and there was gradual a decrease in E% with an increased contact time. But after the first 0.5M NaCl wash, E% increased and had E% above $95 \pm 2\%$ till 160 minutes of the experiment and thereafter had a sharp decrease in E% for the rest of the experimental time. When regeneration cycle was repeated further E% remained constant in subsequent loading process until R4. For R5 and R6 the first 90 minutes had E% of $95 \pm 2\%$ and in 160 minutes there was a slight decrease in E% 85% and for the rest of the experimental time, E% decreased sharply.

From Figure 36 (b), for 0.6-2.0 mm zeolite particle, in R0 the first 45 minutes had 98% removal and E% decreased gradually with an increase in contact time. After 0.5M NaCl wash, E% increased and there was $90 \pm 5\%$ E% till the 120 minutes of the experiment time. Then after, it gradually decreased for the rest of the experiment time. Similar results were obtained until fourth regeneration cycle (R4). Results from R5 and R6 were excluded as volume of NaCl solution was decreased to 2.6 L form 4 L during NaCl wash.

Although, E% increased with regeneration, R0 had higher Q than loading after regeneration cycles in both types of zeolite. 0.2-0.5 mm and 0.6-2.0 mm zeolite types had R0 cumulative Q 20.14 mg/g and 19.18 mg/g respectively. Zeolite particle 0.2-0.5 mm had R1 to R6 average cumulative Q 15.98 mg/g. Similarly, 0.6-2.0mm zeolite particle had R1 to R4 average cumulative Q 13.68 mg/g.

From this experiment, it can be said that NaCl solution can be used for regeneration of zeolite repeatedly. Similar result was obtained by Cooney & Booker, 1999, Rahamani et al, 2009, and Li et al, 2011. According to Li et al, 2011, NaCl regeneration method was superior to acid and heat regenerations. The decrease in E% after 160

minutes and 120 minutes of experiments in R1-R4 regenerations in zeolite types 0.2-0.5 mm and 0.6-2.0 mm respectively is due to less availability of adsorption sites. In zeolite particles 0.2-0.5 mm in R5 and R6 regeneration, there was slight decrease in E% at 160 minutes; it might be due to physical deterioration of zeolite. When zeolite is cyclically used for long duration, zeolite will erode to some extent and it could be overcome by zeolite topping (Cooney & Booker, 1999).

10.4.3.2 HCl regeneration

The effect of HCl regeneration was studied using 2 loading and 1 regeneration cycles in zeolite particle 0.6-2.0 mm. In the experimental results shown in Figure 37, at R0 the first 14 minutes had 100% $\text{NH}_3\text{-N}$ removal and 30 minutes showed E% of 95% and it gradually decreased with an increase in experimental time. After 160 minutes of experimental time, E% was almost constant with E% $30 \pm 5\%$. After HCl wash at R1, E% decreased slightly and the first 14 minutes had E% of 94% and E% decreased steadily and reached 25% in 140 minutes of an experiment time. Qof zeolite decreased drastically after washing the column with 0.5M HCl. R0 and R1 had cumulative Q of 23.57 mg/g and 5.06 mg/g respectively.

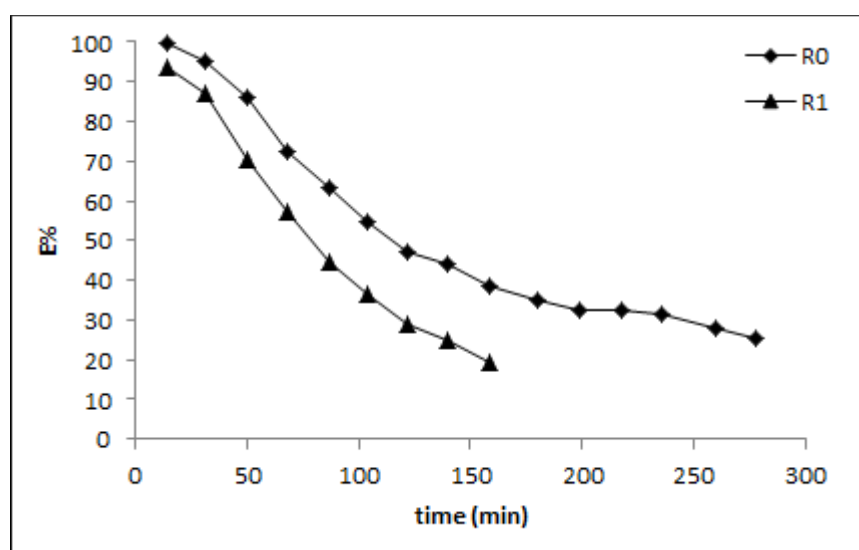


Figure 37: 0.5M HCl regeneration (initial NH_4^+ concentration: 1500 mg/L; particle size: 0.6-2.0 mm, pH: 7.0 ± 0.1 ; flow rate: 15 ml/minute; adsorbent dosage: 300 g; sample volume: 4000 ml)

In HCl regeneration, the adsorption capacity of zeolite decreased after 1st regeneration. It may be because of lower pH, NH_4^+ has to compete with H^+ ions (Erdogan & Ulku, 2011; Hedström, 2001; Huang et al, 2010; Thornton et al, 2007; Englert & Rubio, 2005) and H_3O^+ ions (Li et al, 2011) for the exchange sites. Besides at very low pH (pH 2), zeolites tend to dissolve (Leyva-Ramos et al, 2004; Widiastuti et al, 2011).

11. CONCLUSION

Based on the results, it can be concluded that natural zeolite form Zeocom[®], is suitable for NH₃ removal process in wastewater. NH₃ removal by zeolite depends upon various factors such as particle size, contact time, pH, initial ammonium load, and a flow rate. In both batch and column experiments, smaller zeolite particle size 0.2-0.5 mm showed better Q and E% than zeolite particle size 0.6-2.0 mm as a result of higher surface area. NH₃ removal was faster at initial contact time because of empty adsorption site and a high concentration gradient. Similarly both the experimental set up performed best at neutral pH range irrespective of zeolite particle size.

The NH₄⁺ E% decreased with an increase in TS concentration. It might be because of competition between NH₃ and other particles in slurry for active sites in zeolite. In the column study, a slower flow rate provided better E% and Q; it is because at slower flow rate solution had more contact time with zeolite compared with a higher flow rate. From this observation, it is clear that hydraulic retention time is an important parameter in the IE process.

NaCl can be used to regenerate exhausted column as NH₄⁺ exchange capacity of zeolite was restored after NaCl wash. Besides, the column can be reused even after 6-7 wash. However, HCl regeneration was unable to restore NH₄⁺ removal capacity of zeolite. Therefore, NaCl is the better regenerant compared with HCl. However, the effluent Na concentration after regeneration may pose a problem for effluent disposal. On the positive side, the recovered NH₄Cl is of commercial value and the life span of the zeolite bed is prolonged.

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Appendix

TS in initial sample

Date	TS (mg/l)
7.2.2013	670
8.2.2013	650
12.2.2013	630
13.2.2013	630
14.2.2013	630
15.2.2013	590
19.2.2013	650
20.2.2013	600
25.2.2013	660
26.2.2013	640
11.4.2013	660
24.4.2013	670
26.4.2013	670
16.5.2013	630
20.5.2013	640
29.5.2013	610
30.5.2013	670
6.6.2013	640
24.6.2013	630

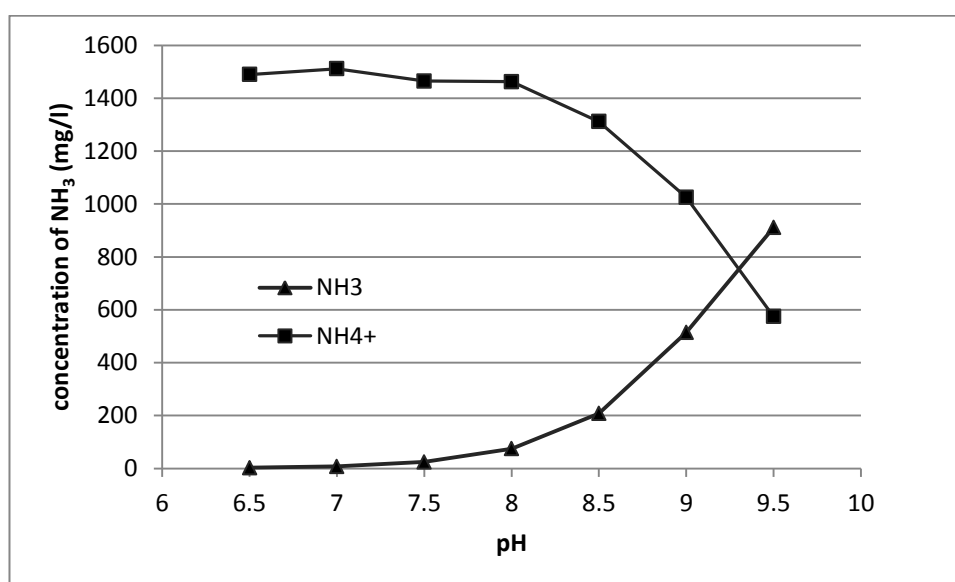


Figure 38: ratio of $\text{NH}_3/\text{NH}_4^+$ at various pH (0.2-0.5mm)

The availability of free $\text{NH}_3/\text{NH}_4^+$ ions at pH range 6.5-9.5 was calculated using equation 11 (Figure 38). From Figure 38, it is clear that at pH 6.5 & 7, NH_4^+ ion was predominating whereas NH_3 concentration was nil. After pH 7, there was gradual decrease in NH_4^+ ion concentration and increase in NH_3 . Around pH 9.3 the concentration of $\text{NH}_3/\text{NH}_4^+$ was equal.